THE UNIVERSITY OF ALBERTA

THE INVESTIGATION OF FREE-RADICAL ACETOXY GROUP
MIGRATION

BY

FRANCIS C. P. LAW

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled, THE INVESTIGATION OF FREE-RADICAL ACETOXY GROUP MIGRATION, submitted by Francis C. P. Law, in partial fulfilment of the requirements for the degree of Master of Science.

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# ABSTRACT

The 2-acetoxy-2-methylpropyl free-radical and the 2-acetoxypropyl free-radical were investigated with the intention of gaining insight into the possibility of the 1,2-acetoxy migration and the mechanism of the proposed rearrangement. The desired radicals were generated by the peroxide initiated decarbonylations of β-acetoxy-β-methylbutyraldehyde and β-acetoxybutyraldehyde. A second method of preparing the same radicals was by the reduction of 1-chloro-2-methyl-2-propyl acetate and 1-chloro-2-propyl acetate with triphenyltin hydride.

Rearrangement is found only in decarbonylation of β-acetoxy-β-methylbutyraldehyde, and the ratio of rearranged product to unrearranged product increases with decreasing initial aldehyde concentrations. This concentration dependence has been used as evidence in establishing that a bridged acetoxy radical is not involved but rather the rearrangement proceeds from a primary radical to a more stable tertiary radical. Explanations were offered in interpreting the lack of observed rearrangement in the other reactions studied.

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# INTRODUCTION

Molecular rearrangements have received a great deal of attention in organic chemistry. Among rearrangements the nucleophilic 1,2 shift, in which a group migrates with its pair of bonding electrons from one atom to an adjacent electron-deficient atom, has received the most attention. Phenyl, alkyl, hydrogen and halogen among other groups undergo 1,2 shifts by carbonium ion intermediates and have been the subject of considerable investigation (1).

Much less studied are 1,2 free-radical rearrangments in which the migrating group moves to an atom bearing an odd electron. Walling (2) in his review of free-radical rearrangments, points out that (at least at ordinary temperature) free radicals show much less tendency to undergo rearrangement than do carbonium ions. In fact, rearrangements involving free-radicals have been known only since 1944 (3). Recently, many investigations of 1,2 free-radical rearrangements from one carbon atom to another have been carried out in solution and the results of these studies have been reviewed for the period 1936 to 1967 (4).

Conflicting views as to the possibility of free-radical rearrangments involving a 1,2 hydrogen shift occur in the literature. Glazebrook and Pearson (5) reported the rearrangement of the <u>iso</u>-propyl radical to the <u>n</u>-propyl radical. These results however, were questioned by Kharasch, Kane, and Brown (6), Masson (7), Chilton and Gowenlock (8), Heller and Gordon (9) and Bellinge and

Gowenlock (10). Kharasch, Lambert,and Urry (11) later reported that treatment of $\gamma$-chloropropylbenzene with *n*-butylmagnesium bromide in the presence of cobaltous chloride gave *trans*-$\beta$-methylstyrene (rather than allylbenzene) and *trans*-but-2-ene (rather than but-1-ene). These products were accounted for by 1,2 hydrogen shifts followed by subsequent disporportionation. However Slaugh

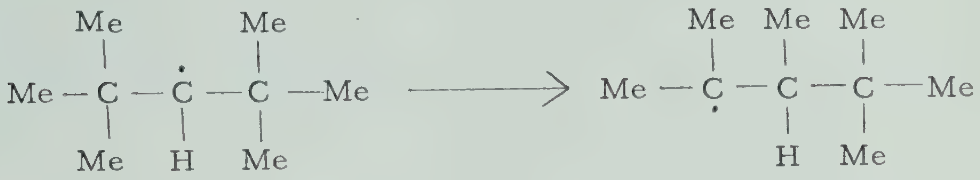
$$C_6H_5CH_2CH_2\dot{C}H_2 \longrightarrow C_6H_5CH_2\dot{C}HCH_3$$

$$CH_3CH_2CH_2\dot{C}H_2 \longrightarrow CH_3CH_2\dot{C}HCH_3$$

(12) suggested that the formation of *trans*-$\beta$-methylstyrene and *trans*-but-2-ene might have been due to subsequent migration of the double bond. The most striking evidence pointing to the absence of 1,2 hydrogen shifts has been obtained by employing labelled atoms (deuterium and tritium) by Curtin and Kauer (13), Brown and Russell (14) and Voevodsky, Lavrovskaya, and Mardaleishvily (15). This evidence indicates that no 1,2 hydrogen shift has been soundly proved and rearrangements of this kind must be considered to be unlikely. Despite this some authors still assume that such a rearrangement is possible (12, 16, 17).

Contrary to the behavior of carbonium ions which often rearrange by the shift of alkyl groups, hydrocarbon radicals in solution are rather stable in this respect. Thus, neopentyl (18) and neohexyl (19, 20) radicals produced by various means fail to give rearranged products. Bromination of 2,2,4,4-tetramethyl-

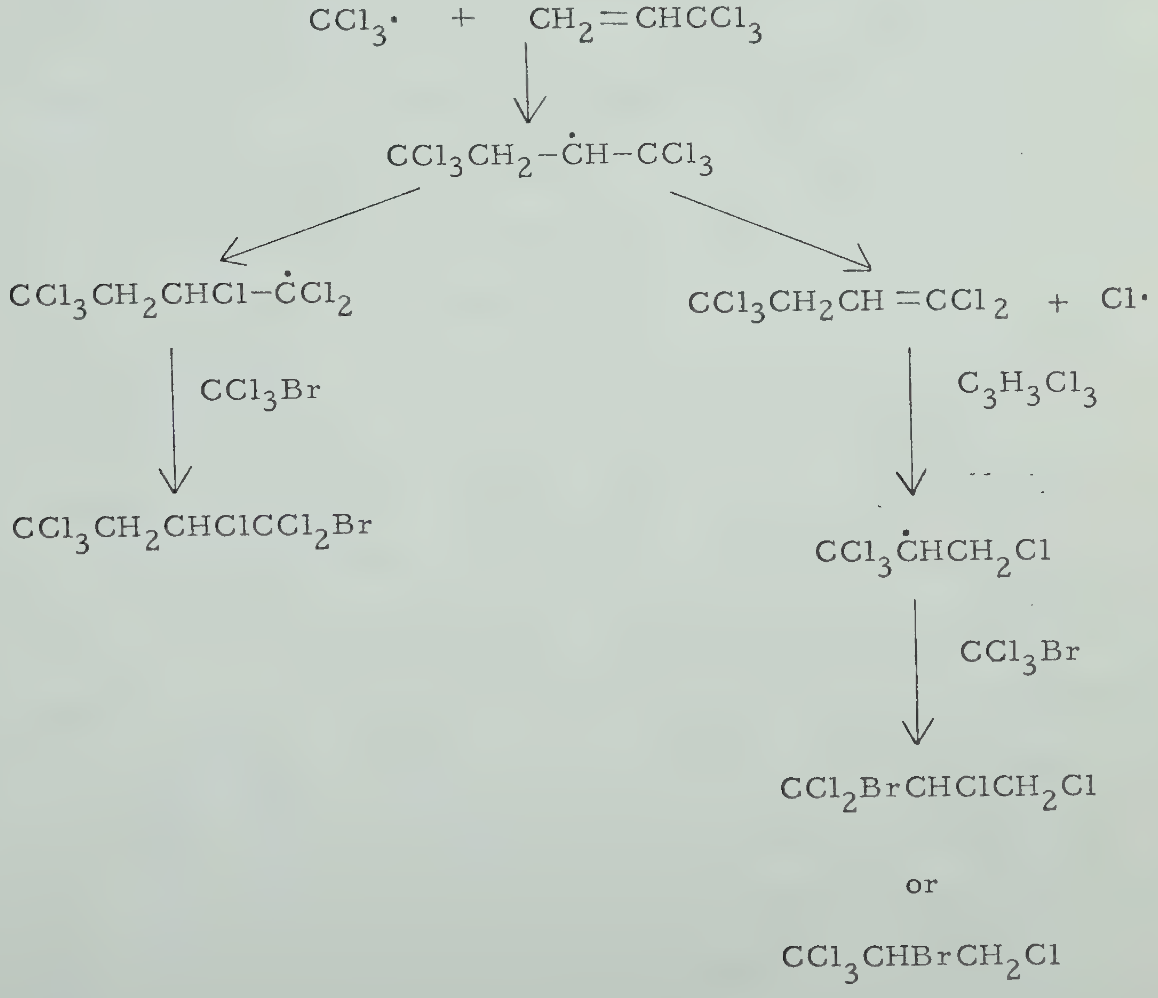
pentane under ultraviolet light at 200° (21) yields a product postulated as 2-bromo-2,3,4,4-tetramethylpentane formed presumably as a result of the rearrangement of the initially formed radical to the tertiary one by a 1,2 shift of the methyl group.



The assignment of the structure of the product, however, has been questioned by Walling (22) and an investigation carried out by Backhurst (23) failed to provide any evidence of such a rearrangement. Dominiguez and Trotman-Dickenson (24) observed the formation of rearranged products in the addition reactions of iso-propyl and t-butyl radicals to acetylene, and also postulated the shift of the methyl group in the intermediate alkenyl radicals. This, however can be explained by rearrangement via a 1,2 vinyl group migration (25). The rearrangement of alkyl radicals with cleavage of C–C bond requires considerable activation energy, and is therefore unlikely to occur in the liquid phase at moderate temperatures (26).

In a series of publications, starting from 1951, Nesmeyanov and his co-workers (26 - 32) have demonstrated the facile 1,2 migration of chlorine in polyhalogenoalkyl radicals in the liquid phase. Kharasch, Rossin, and Fields (33) reported that the peroxide- and light-catalyzed addition of hydrogen bromide to

3,3,3-trichloropropene gave a product different from the known 1,1,1-trichloro-2-bromopropene, which he considered to be 1,1,1-trichloro-3-bromopropene. Subsequently this material has been prepared by another route and Nesmeyanov (26) has shown that the addition product is actually 1,1,2-trichloro-3-bromopropane, suggesting that it is formed via the rearrangement of the radical $CH_2Br\dot{C}HCCl_3$ to $CH_2BrCHCl\dot{C}Cl_2$. Radical additions of mercaptans (34) to trichloropropene also give rearranged products while addition of bromotrichloromethane (35) gives a mixture of products which can be accounted for by the following scheme.



Rearrangements during radical additions to analogs of trichloropropene have also been noted e.g. with 1,1,1-trichloro-2-methylpropene (29), 2,3,3-trichloropropene (30) and 2,3,3,3-tetrachloropropene (30). In these cases the variety of products evidently arises from sequences similar to but more complicated than those shown above (36). Nesmeyanov has also reported (34) that irradiation of 2-bromo-3,3,3-trichloropropene leads to complete isomerization to 1,1,2-trichloro-3-bromopropene. The isomerization also occurs spontaneously on standing and is inhibited by hydroquinone or dimethylaniline, indicating it is a radical chain process. Even more striking examples of radical chain processes which seem explicable only in terms of 1,2 halogen shifts have been described by Urry and Eiszner (37) in the photochemical reaction of diazomethane and many polyhalomethanes. Typical is the reaction with carbon tetrachloride which gives pentaeritritol tetrachloride, $C(CH_2Cl)_4$ in 60% yield. The reaction is evidently a radical chain process since a quantum yield of 300 at 0° has been observed. Analogous products are obtained with bromotrichloromethane, chloroform, and methyl trichloroacetate (37) but brominated and iodinated methanes react differently (38). This is because bromine atom elimination from the $CBr_3CH_2\cdot$ radical occurs more rapidly than rearrangement (39). At lower temperatures the competition between bromine atom migration and elimination apparently becomes more favorable. Thus Skell, Allen, and Gilmour (40) have reported that at -78°, t-butyl hypochlorite chlorination of either n-propyl or

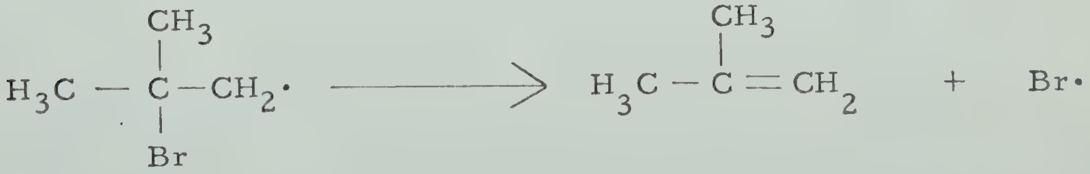
iso-propyl bromide gives 1-bromo-2-chloropropane, and similarly, both iso-butyl and t-butyl bromide give 1-bromo-2-chloro-2-methylpropane. Recently, Haag and Heiba (41) have reported that

$$C_4H_9O\cdot + CH_3CHBrCH_3 \longrightarrow C_4H_9OH + \cdot CH_2CHBrCH_3$$

$$\cdot CH_2CHBrCH_3 \longrightarrow CH_2Br\dot{C}HCH_3$$

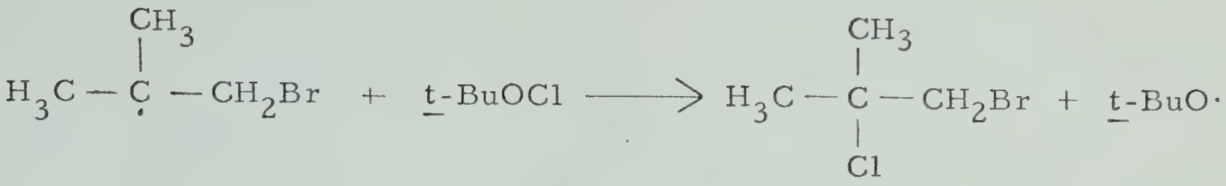
$$CH_2Br\dot{C}HCH_3 + C_4H_9OCl \longrightarrow CH_2BrCHClCH_3 + C_4H_9O\cdot$$

photochlorination of t-butylbromide with t-butylhypochlorite at -78° yields not only 1-bromo-2-chloro-2-methylpropane but also 1-chloro-2-bromo-2-methylpropane. Moreover, the proportion of 1-chloro-2-bromo-2-methylpropane in the reaction products increases with increasing hypochlorite concentrations. These results demonstrate that 2-bromo-2-methylpropyl radical is a true intermediate in the photochlorination and can be intercepted via Cl-transfer from t-butylhypochlorite. The formation of 1-bromo-2-chloro-2-methylpropane was interpreted as the result of bromine atom elimination from the initially formed radical and readdition to the double bond so formed. Evidence for the occurrence of bromine atom



$$H_3C-\underset{Br}{\overset{CH_3}{C}}-CH_2\cdot \longrightarrow H_3C-\overset{CH_3}{C}=CH_2 + Br\cdot$$

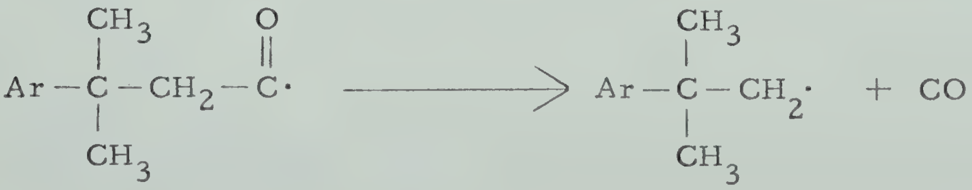
$$H_3C-\overset{CH_3}{C}=CH_2 + Br\cdot \longrightarrow H_3C-\underset{\bullet}{\overset{CH_3}{C}}-CH_2Br$$



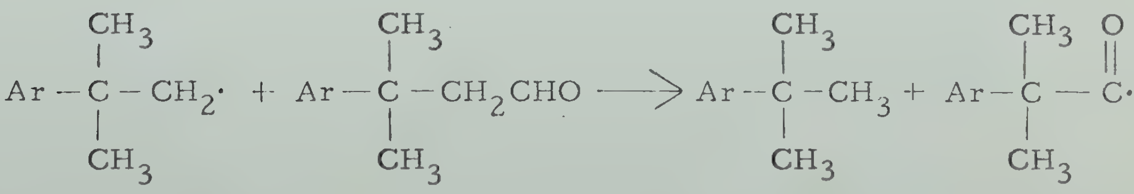
$$H_3C-\dot{C}(CH_3)-CH_2Br + \underline{t}\text{-}BuOCl \longrightarrow H_3C-C(CH_3)(Cl)-CH_2Br + \underline{t}\text{-}BuO\cdot$$

elimination was obtained from the photochlorination of t-butylbromide at -78° in the presence of allene which acted as scavenger for free bromine atoms. The yield of bromochloropropenes were 42% at the expense of 1-bromo-2-chloro-2-methylpropane.

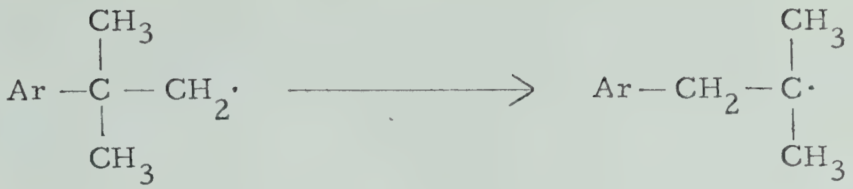
In 1944, Kharasch, Lambert, and Urry (42) showed that treatment of 1-chloro-2-phenyl-2-methyl propane (neophyl chloride) with phenylmagnesium bromide in the presence of cobaltous chloride led to a mixture of hydrocarbons in 55% yield, half of which had rearranged. Later, a similar rearrangement was investigated by Winstein and Seubold (43) who studied the decarbonylation of 3-phenylisovaleraldehyde initiated by di-t-butyl peroxide. They obtained 90% carbon monoxide and 70% of a 1:1 mixture of t-butyl and iso-butyl benzenes, and interpreted the result in terms of the sequence shown in equations A-D. Equation C shows the rearrangement of the intermediate "neophyl" radical by a 1,2 shift of the phenyl group.



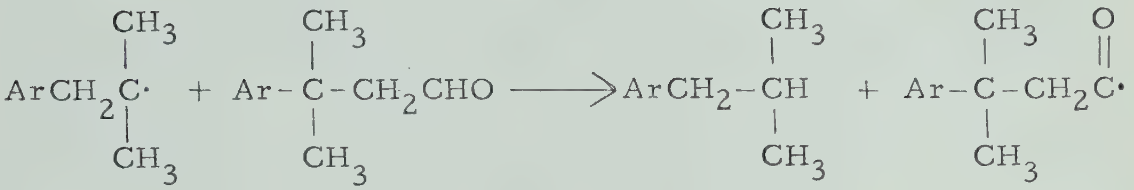
$$Ar-C(CH_3)_2-CH_2-\overset{O}{\overset{\|}{C}}\cdot \longrightarrow Ar-C(CH_3)_2-CH_2\cdot + CO \qquad (A)$$



$$Ar-C(CH_3)_2-CH_2\cdot + Ar-C(CH_3)_2-CH_2CHO \longrightarrow Ar-C(CH_3)_2-CH_3 + Ar-C(CH_3)_2-\overset{O}{\overset{\|}{C}}\cdot \qquad (B)$$

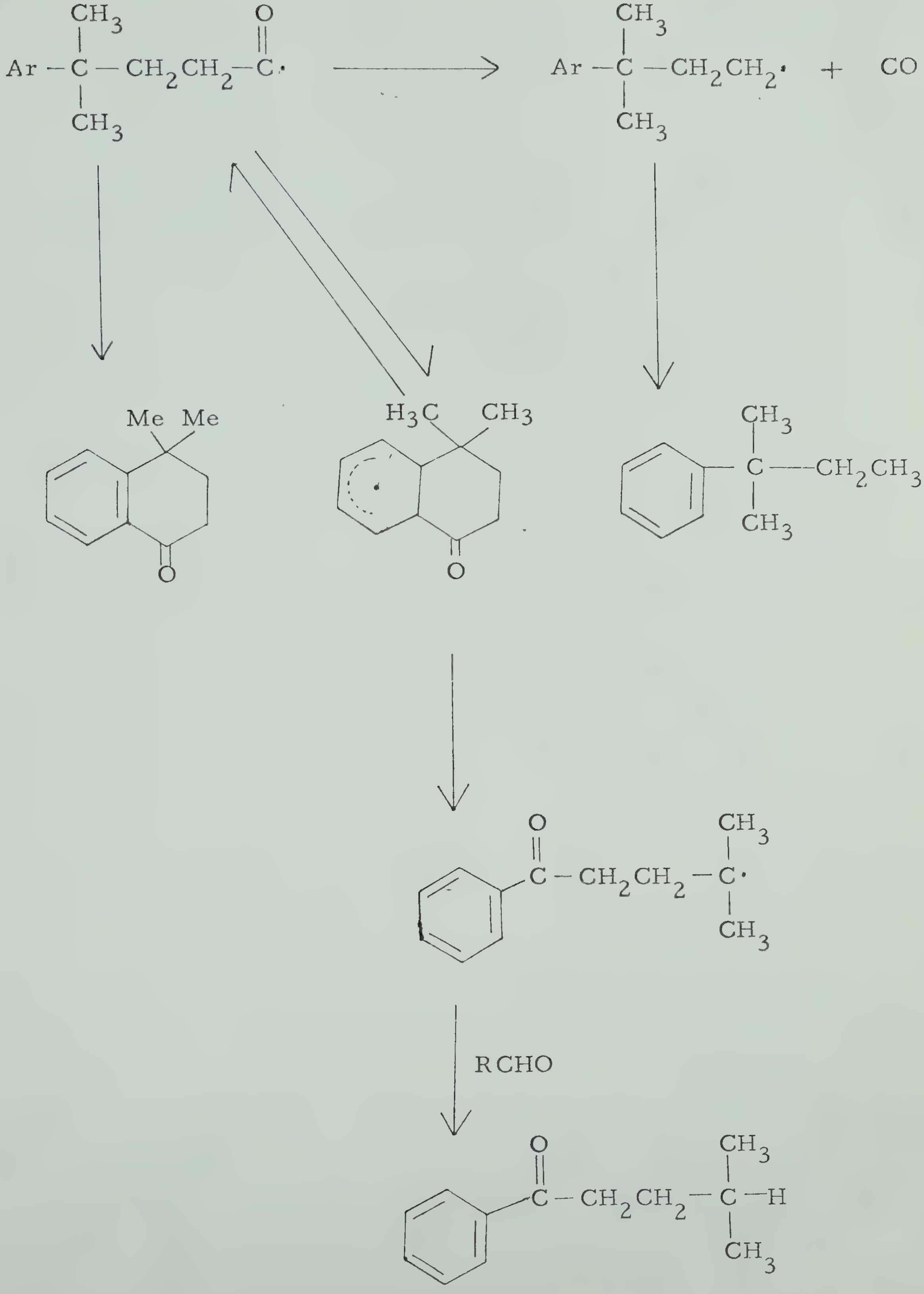


$$Ar-\overset{CH_3}{\underset{CH_3}{C}}-CH_2\cdot \longrightarrow Ar-CH_2-\overset{CH_3}{\underset{CH_3}{C}}\cdot \qquad (C)$$



$$ArCH_2\overset{CH_3}{\underset{CH_3}{C}}\cdot + Ar-\overset{CH_3}{\underset{CH_3}{C}}-CH_2CHO \longrightarrow ArCH_2-\overset{CH_3}{\underset{CH_3}{CH}} + Ar-\overset{CH_3}{\underset{CH_3}{C}}-CH_2\overset{O}{\overset{\|}{C}}\cdot \qquad (D)$$

Subsequently Seubold (20) showed that the decarbonylation and rearrangement are successive steps and that the "neophyl" radical has independent existence. When the concentration of aldehyde increased from 1 M to 6.4 M (pure aldehyde), the ratio of *iso*-butyl- to *t*-butylbenzene increased from 1.3 to 4.0, showing that the rearranged product is concentration dependent. However, the ratio was essentially temperature independent, indicating that equations B and C have comparable activation energies. Recently, Trecker, Hartzler, and Urry (44) found that the free radical chain reaction mechanism proposed (20, 42, 43) was too simple and suggested that a reaction resulting in the formation of ketonic products at lower temperature should be added. For example, the peroxide initiated reaction of 4-methyl-4-phenylpentanal at 100° gives 18% 4,4-dimethyl-1-tetralone and 18% 4-methylvalerophenone and only 30% of the product of decarbonylation 2-methyl-2-phenyl butane.


Ar–C(CH3)(CH3)–CH2CH2–C(=O)·
Ar–C(CH3)(CH3)–CH2CH2· + CO
Me Me
H3C CH3
CH3
C–CH2CH3
CH3
RCHO

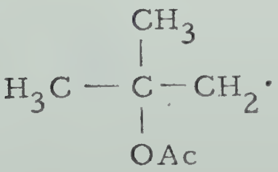
It is to be noted that rearrangement in the opposite direction, namely of the tertiary radical 1,1-dimethyl-2-phenylethyl (prepared by decarbonylation of 2,2-dimethyl-2-phenylpropionic aldehyde) to the primary "neophyl" radical, does not take place (45). The high stability of the product radical is not however, necessarily the driving force for rearrangement, since it has been shown, for example, that 2-phenylethyl-1-$^{14}$C radicals undergo rearrangement to 2-phenylethyl-2-$^{14}$C radicals (46, 47). With the phenylethyl radical there are no structural factors favouring rearrangement.

There are many results pointing to the importance of the lifetime of the radical on the extent of its rearrangement. Thus, Winstein, Heck, Lapporte, and Baird (48), Slaugh (12) and Wilt and Philip (49) have shown that the extent of rearrangement on decarbonylation of aldehydes decreases on addition of a good hydrogen donor e.g. benzyl mercaptan or thiophenol. The chain-transfer constants for mercaptans are known to be considerably higher than those of aldehydes. Therefore, addition of mercaptan decreases the lifetime of radicals so that they are unable to rearrange. Slaugh (12) has proved this point by showing that on decarbonylation of 3-phenylpropanal in the presence of S-tritiobenzyl mercaptan the side chain of the resulting ethylbenzene contained tritium. Seubold (20) has explained the absence of rearrangement (50) in the liquid phase chlorination of t-butylbenzene by sulphuryl chloride as being due to the fact that the reaction of the neophyl radical with sulphuryl chloride is faster than rearrangement.

Recently, the relative migration rates of six aryl groups in the reaction of substituted neophyl chlorides with ethylmagnesium bromide and cobaltous chloride were determined by Ruechardt and Trautwein (51). They found excellent agreement with the values obtained from peroxide-catalyzed decarbonylation of substituted neophyl aldehyde (52).

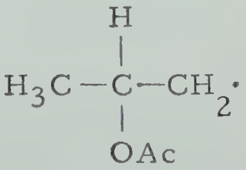
In general, the only groups unambiguously known to undergo intramolecular 1,2 shifts to radical centers are phenyl and chlorine. There is little evidence to support alkyl or hydrogen shifts in known mono-radical systems at ordinary temperatures. However, there is growing evidence for the migration of other unsaturated functions. Several examples of 1,2 vinyl shifts have been reported (53, 54). Similarly, 1,2 acyl migrations, which might be thought of as the oxygen analog of vinyl migration, have been reported in two instances (55, 56).

In view of the considerable interest in the 1,2 free-radical rearrangements, it was decided to investigate the possibility of the occurrence of the previously unknown 1,2 acetoxy shift. The 2-acetoxy-2-methylpropyl radical, (1), and the 2-acetoxypropyl radical, (2), were selected for this study because intramolecular



$H_3C-\overset{CH_3}{\underset{OAc}{C}}-CH_2\cdot$

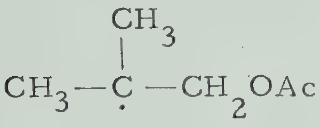
1



$H_3C-\overset{H}{\underset{OAc}{C}}-CH_2\cdot$

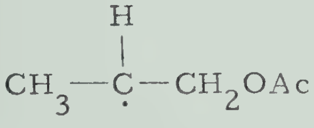
2

migration of acetoxy group from a tertiary carbon atom to a primary carbon atom with the formation of a thermodynamically more stable tertiary, (3), radical could be observed in radical 1 and rearrangement of the same group from a secondary carbon atom to a primary carbon atom with the formation of a secondary, (4), radical could be observed in radical 2.



$CH_3-\overset{CH_3}{\underset{\cdot}{C}}-CH_2OAc$

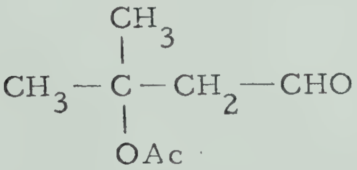
3



$CH_3-\overset{H}{\underset{\cdot}{C}}-CH_2OAc$

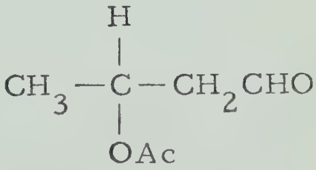
4

The desired radicals were generated by the peroxide initiated decarbonylations of $\beta$-acetoxy-$\beta$-methylbutyraldehyde, (5), and $\beta$-acetoxybutyraldehyde, (6). A second method of preparing



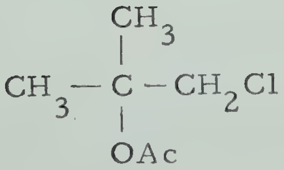
$CH_3-\underset{OAc}{\overset{CH_3}{C}}-CH_2-CHO$

5



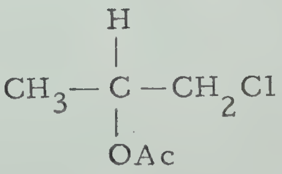
$CH_3-\underset{OAc}{\overset{H}{C}}-CH_2CHO$

6



$CH_3-\underset{OAc}{\overset{CH_3}{C}}-CH_2Cl$

7



$CH_3-\underset{OAc}{\overset{H}{C}}-CH_2Cl$

8

the same radicals was by the reduction of 1-chloro-2-methyl-2-propyl

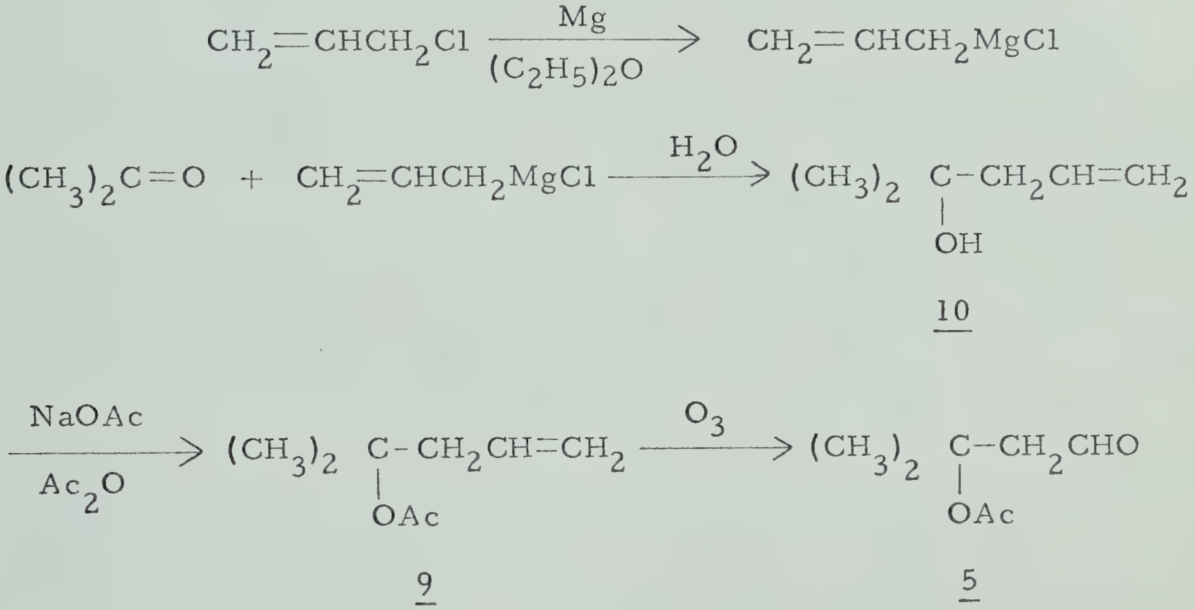
acetate, (7), and 1-chloro-2-propyl acetate, (8), with triphenyltin hydride. A considerable body of evidence has been accumulated by Kuivila and his coworkers (57) establishing the free-radical chain nature of the reduction of organic halides by this reagent.

# RESULTS

## Preparation and decarbonylation of β-acetoxy-β-methylbutyraldehyde, (5).

The aldehyde, 5, was prepared by ozonolysis of 2-methyl-4-penten-2-yl acetate, (9). The procedure followed is outlined in Scheme 1. It was originally hoped to convert the alcohol, 10,

Scheme 1



$$CH_2{=}CHCH_2Cl \xrightarrow[(C_2H_5)_2O]{Mg} CH_2{=}CHCH_2MgCl$$

$$(CH_3)_2C{=}O + CH_2{=}CHCH_2MgCl \xrightarrow{H_2O} (CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}{-}CH_2CH{=}CH_2$$

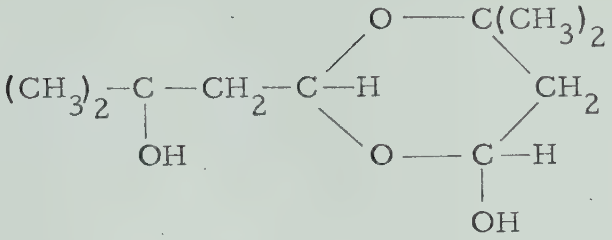
10

$$\xrightarrow[Ac_2O]{NaOAc} (CH_3)_2\underset{\displaystyle OAc}{\underset{|}{C}}{-}CH_2CH{=}CH_2 \xrightarrow{O_3} (CH_3)_2\underset{\displaystyle OAc}{\underset{|}{C}}{-}CH_2CHO$$

9 5

directly to the desired aldehyde by ozonolysis followed by acetylation of the intermediate hydroxyaldehyde. However, ozonolysis gave a mobile liquid which changed rapidly to a wax-like solid which was proposed to be the dimer of β-methylacetaldol, (11). This melted on heating and could be distilled with regeneration of the mobile, monomeric form which solidified within a short time (0.5 - 2 hr) (58). Consequently, this route was abandoned because acetylation of

compound 11 would give the corresponding diacetate.



11

Conversion of 10 to 5 was finally achieved by preparing the olefin, 9, followed by ozonolysis. The acetylation step was carried out at low temperature to prevent elimination and required a reaction time of one day and a large excess of sodium acetate and acetic anhydride. After ozonolysis, the crude product presented another difficulty for partial decomposition resulted from distillation. Purification by glpc at 100° proved unsuccessful for the same reason. Purification by glpc at low temperature (ca. 60°) was successful in getting a more pure compound, however, the process was extremely time consuming and the yield was too little to have any practical value. The least amount of impurities ( ≅ 4%, mainly acetic acid and β-methylcrotonaldehyde) was achieved by using spinning band distillation under vacuum (31 mm).

It was necessary to determine the thermal stability of the aldehyde, 5, and its expected free radical decomposition products, t-butyl acetate and iso-butyl acetate under the conditions that were to be used for the free radical decomposition of the aldehyde, 5.

The results of this study are presented in Table 1.

TABLE I

Thermal Stabilities of *t*-Butyl Acetate, *iso*-Butyl Acetate and *5* with and without Benzoyl Peroxide at 75°.[a]

| Reaction | Reactant[b] (M) | $Bz_2O_2$ M | Products, mole % | | | | |
|---|---|---|---|---|---|---|---|
| | | | $C_4H_7CHO$ | $CH_3COOH$ | *t*-$C_6H_{12}O_2$ | *iso*-$C_6H_{12}O_2$ | Unreacted reactant |
| 1 | *5* (0.7) | - | 9.5 | 3.4 | - | - | 79 |
| 2[c] | *5* (0.7) | 0.08 | 19 | 6.2 | 18 | 3.8 | 46 |
| 3 | *t*-$C_6H_{12}O_2$ (0.5) | - | - | - | - | - | 102 |
| 4 | *t*-$C_6H_{12}O_2$ (0.5) | 0.08 | - | - | - | - | 100 |
| 5 | *iso*-$C_6H_{12}O_2$ (0.5) | - | - | - | - | - | 98 |
| 6 | *iso*-$C_6H_{12}O_2$ (0.5) | 0.08 | - | - | - | - | 101 |

[a] The reactions were carried out in sealed Pyrex ampoules for 3 days.
[b] The solvent was benzene.
[c] Reaction 2 was taken from reaction 9 of Table II.

The aldehyde, 5, was found to decompose thermally only to acetic acid (3.4%) and β-methylcrotonaldehyde (9.5%) (reaction 1), but in the presence of benzoyl peroxide as a free radical initiator t-butyl acetate and iso-butyl acetate were also formed (reaction 2). The latter two compounds were found to be completely stable under the reaction conditions with or without benzoyl peroxide added and the starting acetates (ca. 100%) were recovered after the reaction (reactions 3-6). It was also suspected that iso-butylene could be formed in the reaction and that its reaction with acetic acid would give t-butyl acetate and/or iso-butyl acetate. However, iso-butylene and acetic acid in the presence of benzoyl peroxide under the same reaction conditions produce neither t-butyl acetate nor iso-butyl acetate and both reactants were recovered (see experimental section). This was proved by comparing the glpc analyses before and after the addition of authentic acetates to the reaction mixture.

Having carried out this preliminary study and found that two isomeric acetates were obtained, a detailed study of the reaction was performed. The same reaction conditions were used as in the preliminary study. The results of this study are presented in Table II. Chlorobenzene was originally used as the solvent (reactions 11, 13, and 15) because it is known to be relatively inert to free radical attack (59). Benzene was later used as the solvent (reactions 7-10, 12, and 14) because a better material balance could be obtained (see next section). The concentrations of the starting aldehyde, 5, were varied because we wished to investigate whether the ratios of

## TABLE II

Products from Peroxide Initiated Decarbonylation[a] of $\beta$-Acetoxy-$\beta$-methylbutyraldehyde, (5).[b]

| Reaction | 5 $\times 10^2$M | Solvent | Product concn., $\times 10^2$M $C_4H_7CHO$ | $CH_3COOH$ | t-$C_6H_{12}O_2$ | iso-$C_6H_{12}O_2$ | Unreacted 5 | Ratio $\frac{\text{iso-}C_6H_{12}O_2}{\text{t-}C_6H_{12}O_2}$ |
|---|---|---|---|---|---|---|---|---|
| 7 | 270.0 | $C_6H_6$ | 44 | 16 | 26 | 2.5 | 108 | 0.09 |
| 8 | 94.06 | $C_6H_6$ | 15 | 4.7 | 17 | 2.9 | 52 | 0.17 |
| 9 | 71.31 | $C_6H_6$ | 14 | 4.4 | 13 | 2.7 | 33 | 0.20 |
| 10 | 50.38 | $C_6H_6$ | 6.2 | 2.0 | 5.2 | 1.4 | 31 | 0.27 |
| 11 | 50.20 | $C_6H_5Cl$ | - | 4.2 | 5.3 | 1.3 | 22 | 0.25 |
| 12 | 19.11 | $C_6H_6$ | 4.4 | 1.0 | 1.5 | 0.6 | 4.4 | 0.43 |
| 13 | 18.80 | $C_6H_5Cl$ | - | 2.0 | 1.4 | 0.8 | 11 | 0.57 |
| 14 | 10.76 | $C_6H_6$ | 3.3 | - | 0.7 | 0.5 | 1.8 | 0.71 |
| 15 | 10.69 | $C_6H_5Cl$ | - | - | 0.5 | 0.4 | 6.5 | 0.80 |

[a] The reactions were carried out in selaed Pyrex ampoules at 75° for 3 days.

[b] Each reaction mixture consisted of 5 and benzoyl peroxide (0.08 M).

iso-butyl acetate to t-butyl acetate in the product were dependent on the initial concentrations of the starting aldehyde. These ratios were found to increase from 0.09 to 0.66 as the concentrations of aldehyde 5 in benzene decreased from $207.0 \times 10^{-2}$ to $10.78 \times 10^{-2}$ M. Acetic acid was present in all samples except the most dilute one. iso-Butylene was not detected among the products in any of the reactions. This again was proved by comparing the glpc analyses before and after the addition of iso-butylene gas into each reaction mixture.

When chlorobenzene was the solvent (reactions 11, 13, and 15) only a poor material balance could be obtained. The reason for this is that β-methylcrotonaldehyde, the elimination product of aldehyde 5, could not be detected in the reaction mixtures because it could not be separated from chlorobenzene on any of the glpc columns used. Attempts to utilize the UV spectrum to estimate β-methylcrotonaldehyde concentration was unsuccessful since chlorobenzene and β-methylcrotonaldehyde absorb at approximately the same frequency. The reactions were repeated in benzene (reactions 7-10, 12, and 14) and 95% of the starting aldehyde, 5, was accounted for in the most concentrated sample.

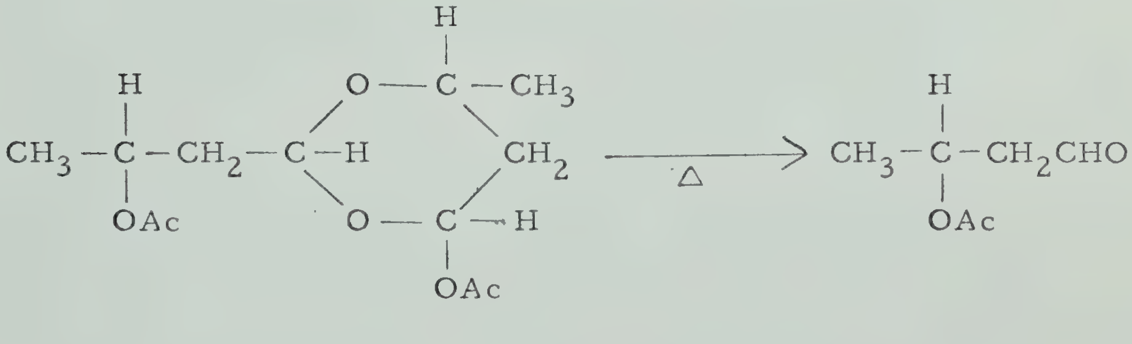
The selection of glpc columns for the analysis of the reaction mixture presented another difficulty. Among more than ten columns attempted, the most satisfactory analyses were obtained by columns made of 10% Ucon Polar, 10% SE-30, and 3% SF-96. However, none of these columns could separate all the compounds

present in each reaction. Two columns, 10% Ucon Polar and 3% SF-96, were therefore used for the analysis of each reaction mixture.

Preparation and decarbonylation of β-acetoxybutyraldehyde (6).

Having found that acetoxy group on a tertiary carbon atom underwent 1,2 migration to a primary carbon atom, we wished to investigate the possibility of acetoxy group rearrangement from a secondary carbon atom to a primary carbon atom.

The aldehyde, 6, had previously been prepared in 1943 by decomposing the diacetate of the dimeric aldol, (12), at 210° and 50 Torr. (60). However the overall yield was very low due to the difficulty in making this compound.



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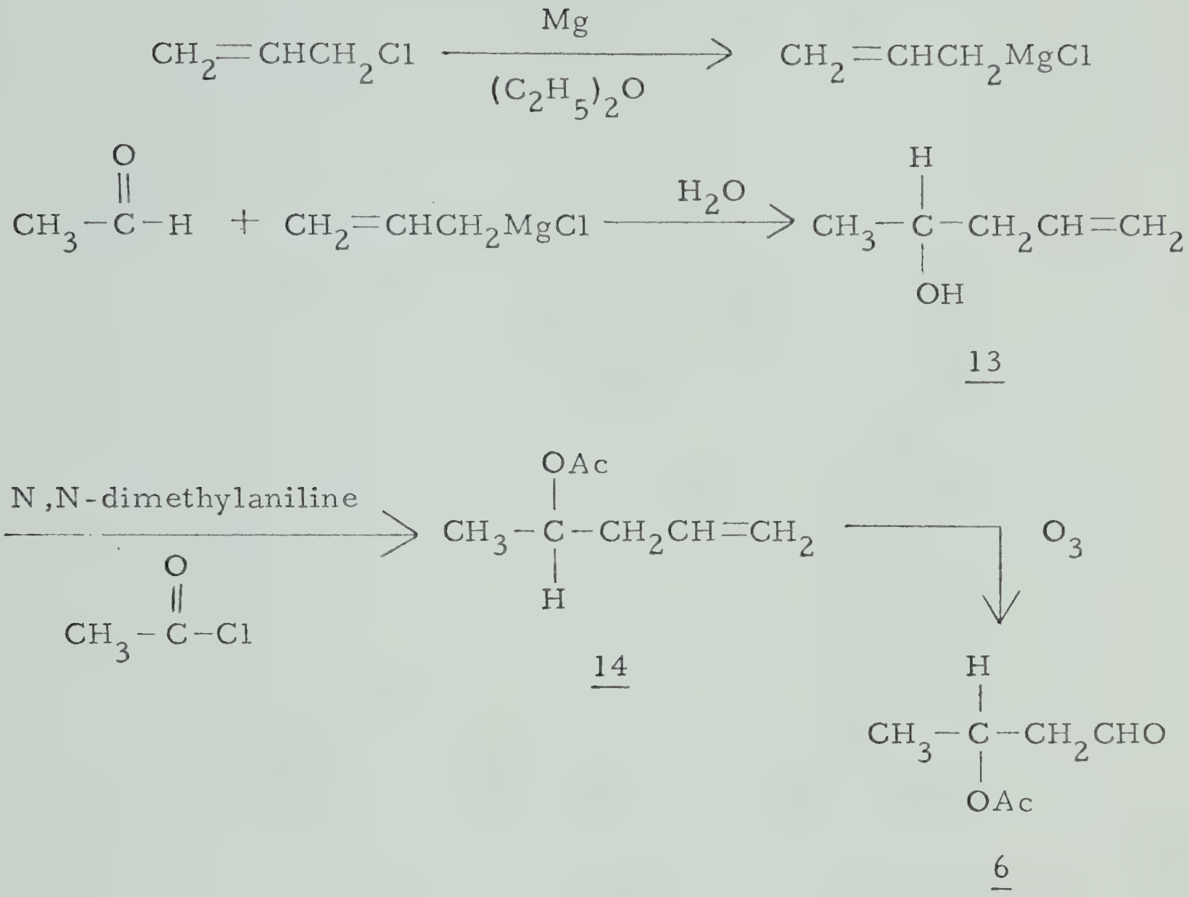
It was necessary to prepare pure monomeric aldol or dimeric aldol from commercially available aldol by drying with calcium chloride and repeated distillation (61). This was a complete failure because the distillate was a viscous mixture of compounds and

polymer which could not be identified. Aldol prepared from two other methods (62, 63) gave no better results. Acetylation of the impure aldol was carried out as by Späth (60) but no analytical means could be found to identify the product as the desired diacetate of the dimeric aldol. These difficulties prevailed because acetaldol exists in many forms (64-69) and distillation of sample of commercial acetaldol or acetaldol which had been permitted to age for several weeks gave resins and distillates containing unsaturated compounds (70). An extremely small amount of pure monomeric acetaldol has been obtained by distilling freshly prepared aldol under reduced pressure as rapidly as possible (71), but it is not feasible in a large scale synthesis as ours.

The problem of dimerization of the starting material resembled that encountered in the preparation of compound 5. A similar synthetic method was therefore used. This is outlined in Scheme 2. Acetylation by acetyl chloride in N,N-dimethylaniline was used (72). This method gives a better yield and shorter reaction time than acetylation by sodium acetate and acetic anhydride. Peroxide initiated decarbonylation of the aldehyde, 6, was carried out in exactly the same way as the decarbonylation of compound 5. Table III shows all the products obtained.

An anomalously large amount of elimination product, crotonaldehyde, was formed from aldehyde 6 compared with the amount of elimination product observed for compound 5. Acetic

Scheme 2



acid was present in all samples but in smaller quantities than crotonaldehyde. A small amount of iso-propyl acetate was found as a product in these reactions but n-propyl acetate could not be identified in any of the reaction. This was proved by glpc analyses before and after the addition of n-propyl acetate to the reaction mixture. Consequently no evidence for a free radical rearrangement was obtained in this system. Between 78-88% of the starting aldehyde

## TABLE III

Products from Peroxide Initiated Decarbonylation[a] of β-Acetoxybutyraldehyde (6)[b].

| Reaction | 6 | Product concn., x $10^2$ M | | | | |
|---|---|---|---|---|---|---|
| | x $10^2$ M | $C_3H_5CHO$ | $CH_3COOH$ | iso-$C_5H_{10}O_2$ | n-$C_5H_{10}O_2$ | Unreacted 6 |
| 16 | 46.46 | 12.0 | 5.1 | 1.7 | 0.0 | 17.4 |
| 17 | 34.37 | 9.8 | 3.4 | 1.1 | 0.0 | 13.1 |
| 18 | 3.96 | 1.0 | 0.3 | 0.1 | 0.0 | 2.1 |

[a] The reactions were carried out in sealed Pyrex ampoules at 75° for 3 days.

[b] Each reaction mixture consisted of 6 and benzoyl peroxide (0.08 M).

, 6, was accounted for as either products or unreacted aldehyde. The products are listed in Table III.

An alternative method of generating free radicals suitable for rearrangement was now attempted. The reduction of alkyl chloride with triphenyltin hydride has been shown to be a free radical process (57) and generates free radical by the mechanism which will be discussed in more detail later. In order to make the desired radicals to try to observe rearrangement, it was first necessary to prepare the appropriate chlorides and triphenyltin hydride.

### Preparation of triphenyltin hydride.

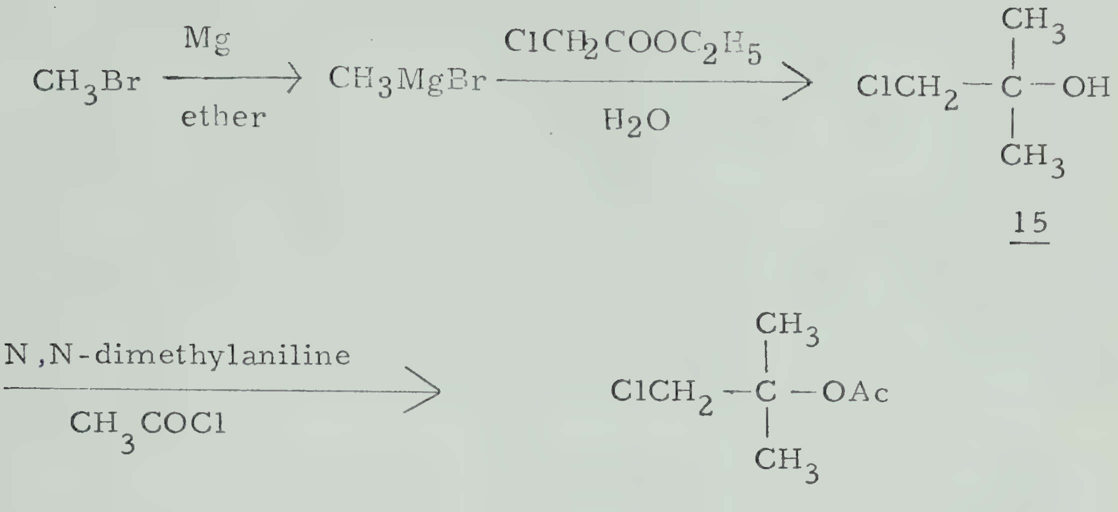
Kuivila (73) prepared triphenyltin hydride by reduction of triphenyltin chloride with lithium aluminum hydride in ether.

$$\varphi_3\mathrm{SnCl} \xrightarrow[\text{ether}]{\mathrm{LiAlH_4}} \varphi_3\mathrm{SnH}$$

### Preparation and photo-initiated reduction of 1-chloro-2-methyl-2-propyl acetate, (7), with triphenyltin hydride.

The chloride, 7, was obtained from the corresponding alcohol, 15, using a modified procedure of Palomma (74) (Scheme 3). Alcohol 15 was prepared by adding an ethereal solution of ethyl chloroacetate to a solution of methylmagnesium bromide. Acetylation was carried out by acetyl chloride in N,N-dimethylaniline

Scheme 3



$$CH_3Br \xrightarrow[\text{ether}]{Mg} CH_3MgBr \xrightarrow[H_2O]{ClCH_2COOC_2H_5} ClCH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH$$

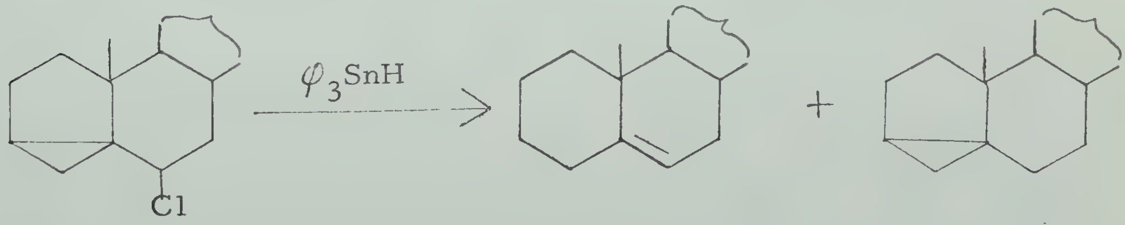
15

$$\xrightarrow[CH_3COCl]{\text{N,N-dimethylaniline}} ClCH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OAc$$

7

as reported by Hauser (72). Purification of the chloride, 7, was best carried out by distillation at reduced pressure.

Recently, Cristol and Barbour (75) reported that reaction of 3,5-cyclochlolestan-6-yl chloride, (16), with triphenyltin hydride gives a mixture of 5-chloestene, (17), and 3,5-cyclochloestane, (18). The results have been interpreted in terms of the formation of intermediate classical radicals which have the option or rearrangement or capture of hydrogen atom from triphenyltin hydride. The ratios of 17 to 18 increase as the concentrations of the triphenyltin hydride decrease when reacting with the same concentration



16 17 18

($\cong$80 mole %) of chloride, 16. They suggested that the lifetime of the radical before chain transfer is increased with lower hydride concentrations and there is therefore more opportunity for the occurrence of radical rearrangement.

The reduction of the chloride, 7, was carried out at progressively lower hydride concentrations in order to lengthen the lifetime of the radical before chain transfer as in Cristol's experiment (75).

The experiment was first performed without AIBN (azobisisobutyronitrile) at various temperatures and with UV light (quartz ampoule was used). Glpc analyses of the resultant reaction mixtures showed no reduction occurred under these conditions.

Kuivila (76) has found that AIBN is necessary to act as an initiator in the reduction of simple alkyl halides by triphenyltin hydride. AIBN (1.5 mole %) was therefore added as a free radical initiator which was decomposed photolytically. When triphenyltin hydride was dissolved in n-pentane, a small amount of white precipitate was observed. This was the decomposition product of triphenyltin hydride (77) and will be discussed in more detail. As the reaction proceeded more and more fine white solid accumulated at the bottom and on the inner surface of the ampoule. Frequent shaking was employed to ensure a constant flux of light reached the solution. The products of the reaction are listed in Table IV, from which it may be seen that in all cases t-butyl acetate was the sole reaction product and in no case was the rearranged product, iso-butyl acetate, formed

## TABLE IV

Product from Reduction[a] of 1-Chloro-2-methyl-2-propyl Acetate, (7), with Triphenyltin Hydride.[b]

| Reaction | 7 x $10^2$ M | $(C_6H_5)_3SnH$ x $10^2$ M | AIBN x $10^2$ M | Product, mole % | |
|---|---|---|---|---|---|
| | | | | t-$C_6H_{12}O_3$ | iso-$C_6H_{12}O_2$ |
| 19 | 1.34 | 66.56 | 8.22 | 40.5 | 0.0 |
| 20 | 0.18 | 31.08 | 1.10 | 16.0 | 0.0 |
| 21 | 0.19 | 14.13 | 0.37 | 12.7 | 0.0 |
| 22 | 0.19 | 7.71 | 0.37 | 7.7 | 0.0 |

[a] The reactions were carried out in selaed Pyrex ampoules at 0° for one week.

[b] The solvent was n-pentane.

(reactions 19-22). The absence of iso-butyl acetate was verified by comparing the glpc analyses before and after the addition of authentic iso-butyl acetate to the reaction mixture.

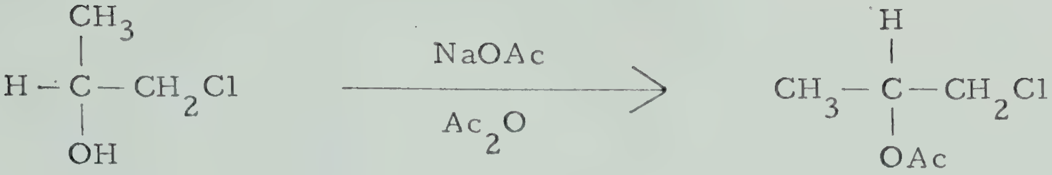
The stabilities of t-butyl acetate and iso-butyl acetate were also determined under the reaction conditions used for the reduction of the acetate, 8. The two compounds were found to be completely stable and all starting acetates were recovered after the reaction (see experimental section).

It was also suspected that the absence of iso-butyl acetate in the reaction product was due to the high concentration of triphenyltin hydride. Photo-initiated reduction was therefore carried out by adding triphenyltin hydride at an extremely slow rate ($7 \times 10^{-9}$ M/min.) to a solution of the acetate, 8, in n-pentane (see high dilution experiment). Once again the only product found was t-butyl acetate.

Since no iso-butyl acetate was observed in any reaction, and t-butyl acetate and iso-butyl acetate in the presence of triphenyltin hydride were stable under the reaction conditions, no further endeavour at material balance was attempted.

## Preparation and reduction of 1-chloro-2-propyl acetate, (8), with triphenyltin hydride.

The desired chloride, 8, was obtained from the corresponding alcohol which was available commerically. The purpose of this experiment was to test the conclusion drawn from the peroxide initiated decomposition of aldehyde 6 that a secondary acetoxy group



$$H-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}-CH_2Cl \xrightarrow[Ac_2O]{NaOAc} CH_3-\overset{\displaystyle H}{\underset{\displaystyle OAc}{C}}-CH_2Cl$$

8

does not undergo 1, 2 migration. Reduction was carried out in the same way as the reduction of chloride 7. iso-Propyl acetate was the only product obtained even with extremely dilute triphenyltin hydride concentration. The products are presented in Table V. The absence of n-propyl acetate was also verified by comparing the glpc analyses before and after the addition of authentic n-propyl acetate to the reaction mixture.

TABLE V

Product from Reduction [a] of 1-Chloro-2-propyl Acetate, (8), with Triphenyltin Hydride. [b]

| Reaction | 8 | $(C_6H_5)_3SnH$ | AIBN | Product, mole % | |
|---|---|---|---|---|---|
| | $\times 10^2$ M | $\times 10^2$ M | $\times 10^2$ M | iso-$C_5H_{10}O_2$ | n-$C_5H_{10}O_2$ |
| 23 | 0.16 | 27.69 | 1.42 | 5.2 | 0.0 |
| 24 | 0.16 | 5.60 | 1.42 | 3.8 | 0.0 |
| 25 | 0.16 | 1.81 | 1.42 | 1.1 | 0.0 |
| 26 | 0.16 | 1.01 | 1.42 | 0.6 | 0.0 |

[a] The reactions were carried out in sealed Pyrex ampoules at 0° for one week.

[b] The solvent was n-pentane.

# DISCUSSION

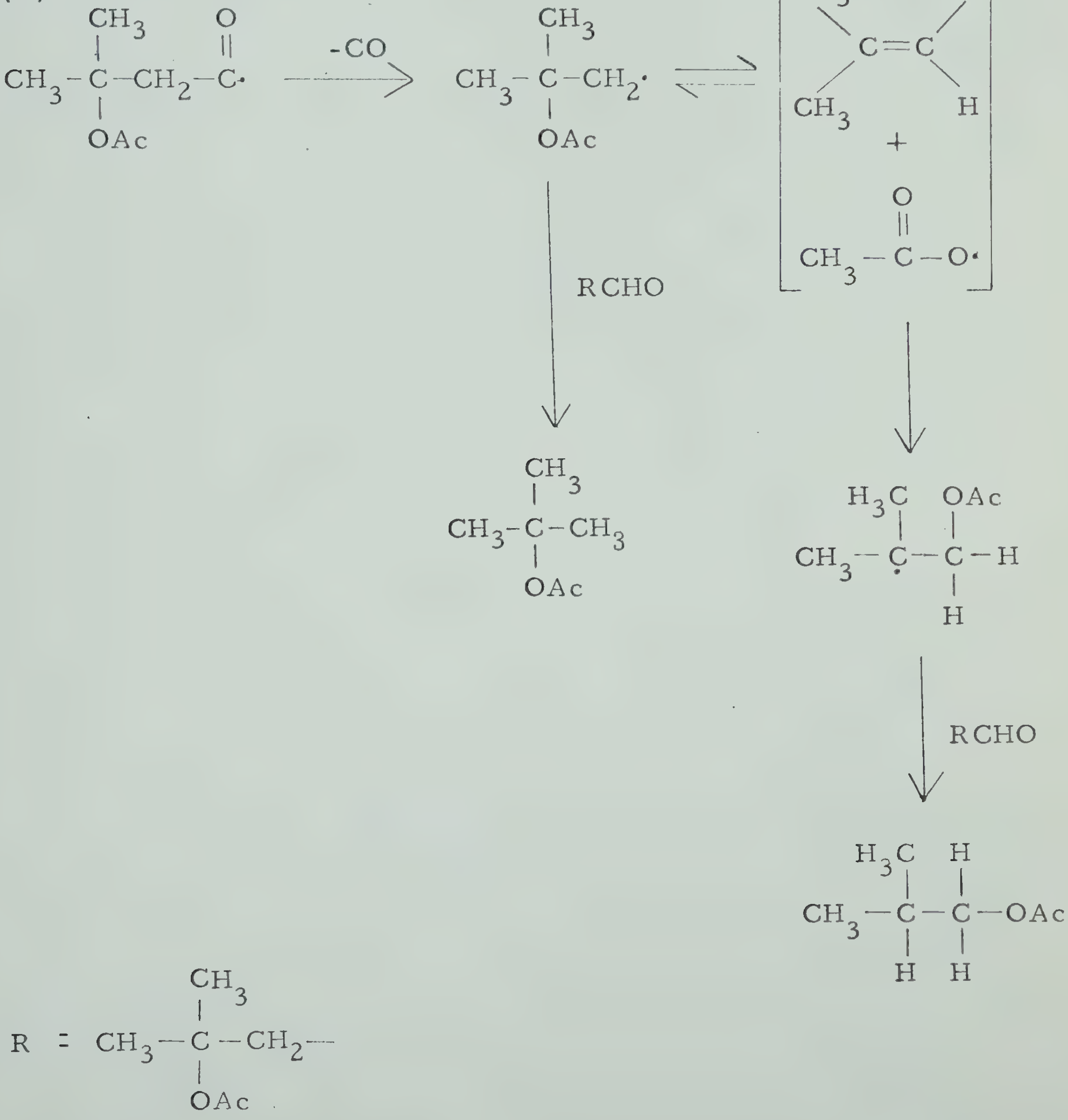
Peroxide initiated decarbonylations of aldehydes have been widely used in generating radicals of known structures and in studying the possibility of rearrangements (12, 20, and 43-50). The mechanism of decarbonylation has been cited in some detail in the introductory section.

The results in Table I show that aldehyde 5 (reaction 1) at 75° without benzoyl peroxide gives acetic acid and β-methylcrotonaldehyde only. In the presence of benzoyl peroxide under the same reaction conditions (reaction 2), decarbonylation of the aldehyde, 5, yields t-butyl acetate and iso-butyl acetate in addition to these elimination products. t-Butyl acetate and iso-butyl acetate are thermally stable under the reaction conditions even with the addition of benzoyl peroxide (reaction 3-6). Also, iso-butylene and acetic acid in the presence of benzoyl peroxide produce neither t-butyl acetate nor iso-butyl acetate. Thus the formation of t-butyl acetate and iso-butyl acetate is the result of free-radical decarbonylation of the aldehyde, 5, and no secondary reactions occur after their formation. Since no iso-butylene was found in any reaction, it follows that radical 1, radical 3, t-butyl acetate, and iso-butyl acetate must all be stable towards elimination. Therefore, elimination occurs exclusively from the aldehyde, 5.

Having found that rearrangement could indeed occur in the system under study, further experiments were carried out to deter-

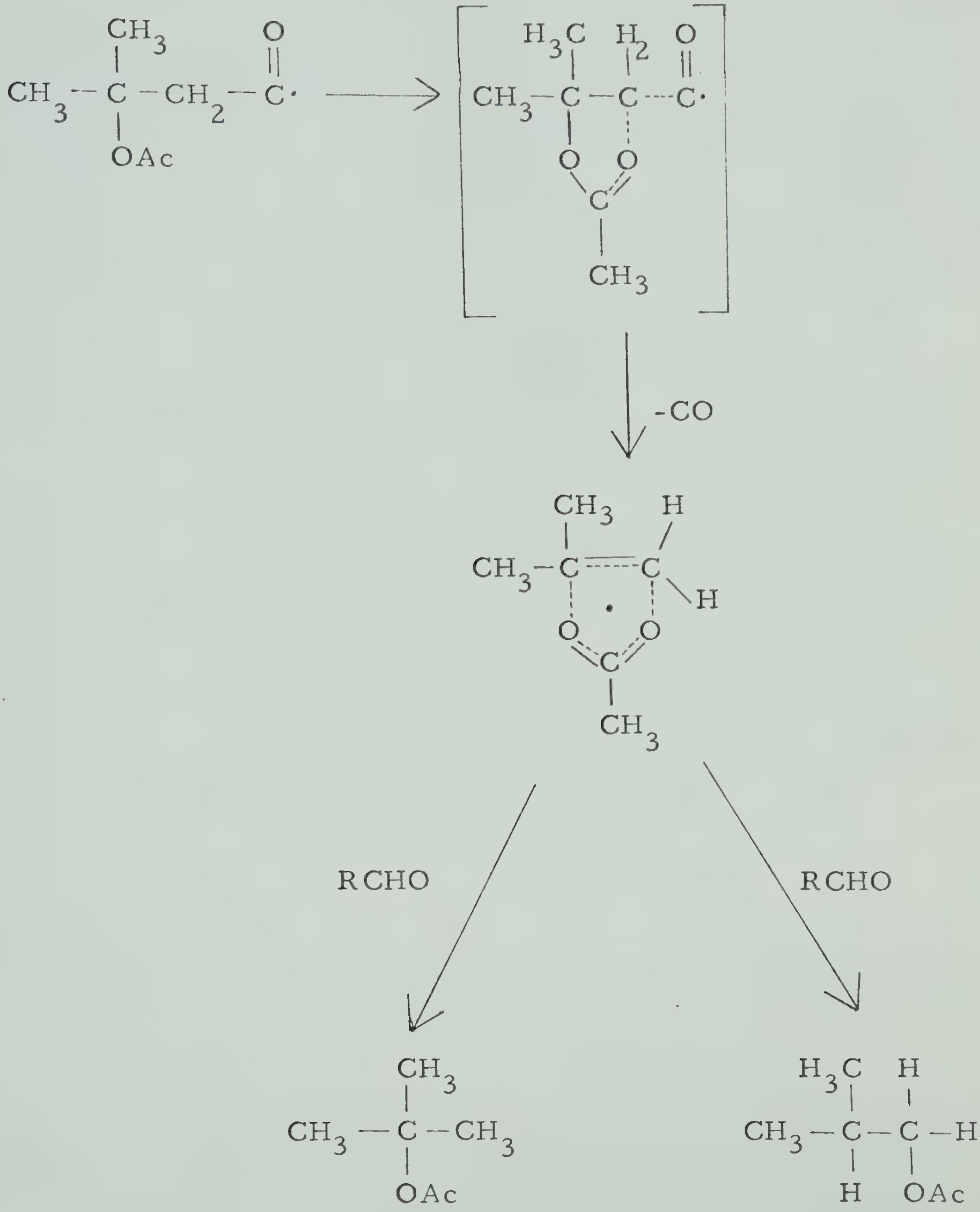
mine the mechanism of the rearrangement process. At least three different modes of radical rearrangement can be formulated to explain the formation of iso-butyl acetate and t-butyl acetate from decarbonylation of the aldehyde, 5.

(A)

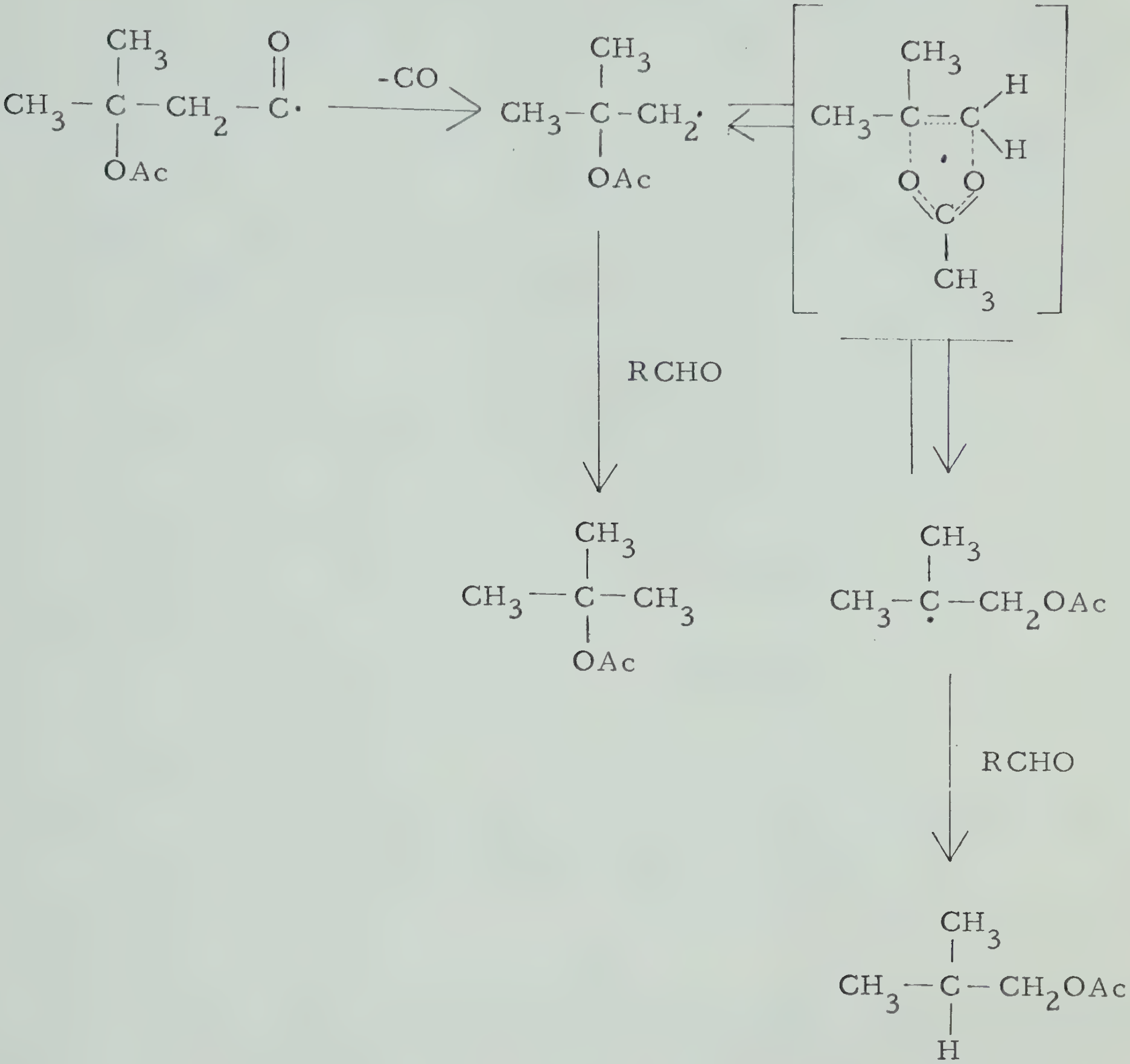


$$R = CH_3-\underset{\displaystyle OAc}{\overset{\displaystyle CH_3}{C}}-CH_2-$$

(B)



(C)



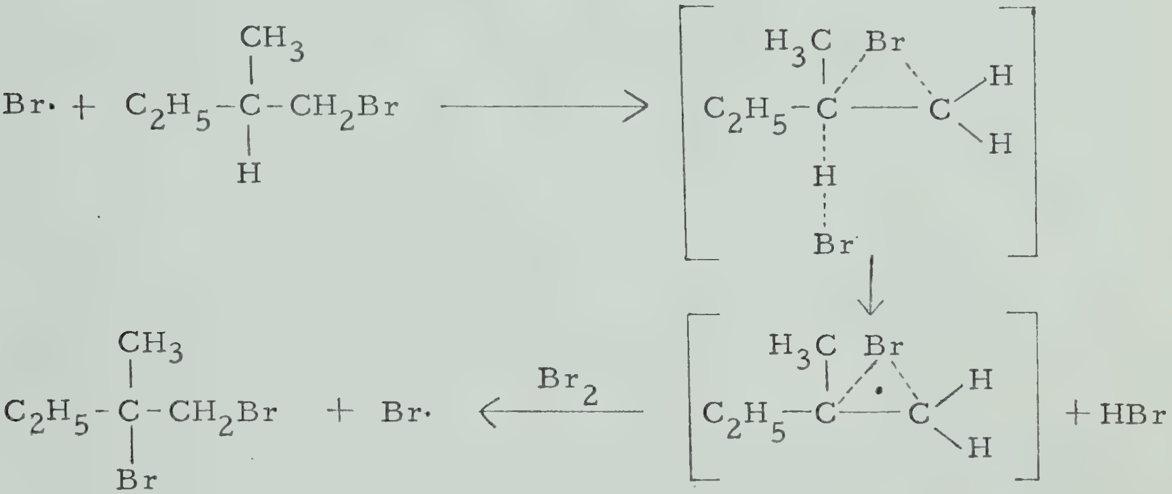
Mode A is a two step process consisting of fragmentation to an acetoxy radical and an olefin followed by recombination to give the rearranged radical, 3. We may exclude this mechanism as the rearrangement pathway because iso-butylene is detected in neither the thermal decomposition of the aldehyde, 5, nor in reduction of the chloride, 7, by triphenyltin hydride. If mode A were operative, a certain amount of olefin might be expected to escape recombination

and should be detected in the product. Furthermore the rate constant for decarboxylation of acetoxy radical at $60^{o}$ is calculated to be $1.6 \times 10^{9}$ $sec^{-1}$ (half-lifetime of the acetoxy radical $4.3 \times 10^{-10}$ sec) (78), and the rate constant of radical additions to vinyl monomers is usually less than $10^{5}$ l. $mole^{-1}sec^{-1}$ (79). Since the two rate constants differ by nearly $10^{5}$, addition of acetoxy radical to iso-butylene is unlikely to occur. This rationalization may not be absolutely correct, because $\pi$ complex formation between acetoxy radical and cyclohexene rather than a direct radical addition to the double bond (80) has been proposed as the intermediate in acetoxy radical addition to cyclohexene (81).

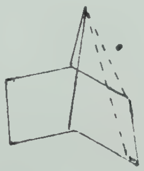
Both mode B and mode C are intramolecular processes. They differ from each other in that mode B represents an intermediate or energy minimum while mode C represents the transition state or energy maximum along the route by which radical $\underline{1}$ rearranges to radical $\underline{3}$.

Skell, Tuleen, and Radio (82) have suggested the existence of non-classical radical intermediates. They found that bromination of 1-bromo-2-methylbutane differs from chlorination of the corresponding chloride in two important respects. First, bromination is selective and yields only 1,2-dibromo-2-methylbutane, whereas chlorination is a reaction of low discrimination and all possible dichlorides are produced. Second, bromination of (+)-1-bromo-2-methylbutane yields (-)-1,2-dibromo-2-methylbutane of high optical purity, whereas chlorination of optically active (+)-1-chloro-2-

methylbutane produced inactive 1,2-dichloro-2-methylbutane. These differences have been interpreted in terms of a mechanistic scheme wherein the bromine substituent assists the departure of the tertiary hydrogen atom. This assistance manifests itself in the formation of a bridged radical, which is capable of maintaining its stereochemical configuration until reaction with molecular bromine occurs. Recently, Warkentin and Sanford (83) report the evidence that 7-norbornenyl is a non-classical radical, since reduction of



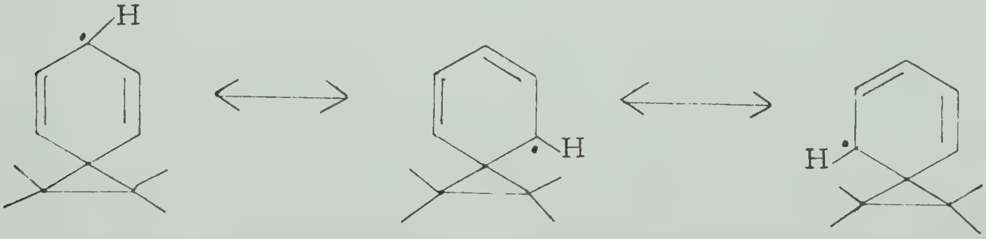
either syn- or anti-7-bromonorbornene with tri-n-butyltin deuteride in hexane leads to the same 7-deuterionorbornene. The yield is



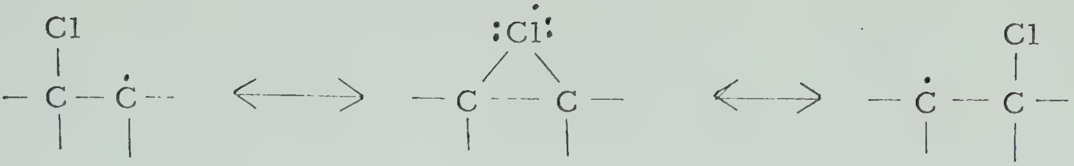
about 80% and there are no other volatile products.

Walling (84) has made an attempt to elucidate why in some

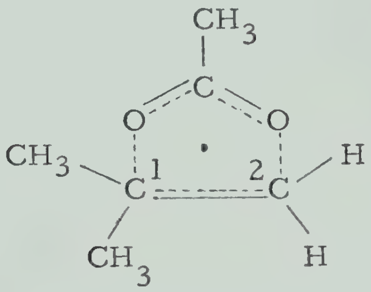
cases the rearrangement involves 1,2 shift (aryl, chlorine) and in the other cases does not (alkyl, hydrogen) by assuming the possibility of intermediate formation of a triangular "non-classical" radical. The rearrangement of radicals always competes with the other possible conversions such as dimerization, disproportionation, decomposition with the formation of a molecule and a smaller radical, intermolecular reaction chain transfer etc., Therefore, it was argued, the triangular state must be less energetic than the transition states for these processes, and hence must be stabilized by the delocalization of the odd electron. As to the formation of intermediate non-classical radicals with 1,2 shift of aryl group, the evidence and suggestions available in the literature, as well as Walling's treatment of this point, seem plausible enough. It was postulated that the transition state is stabilized by delocalization of the odd electron, and by the formation of a new $\sigma$-bond in the cyclopropane ring. Walling has also suggested that, with chlorine



shift, the intermediate might be stabilized by an expanded valence shell for chlorine.



It should be possible in principle to distinguish modes B and C by carrying out decarbonylation at various initial concentrations of the aldehye, 5. If mode B were operative, the non-classical radical formed is a resonance stabilized species. It will therefore be subjected to transfer at $C_1$ and $C_2$ to the same relative extent



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whatever the concentration of the hydrogen atom donor (aldehyde 5) and the ratio of t-butyl acetate to iso-butyl acetate should remain constant. On the other hand, mode C requires a competition between hydrogen abstraction by radical 1 and rearrangement of radical 1 to radical 3. Therefore slow chain transfer rates i.e. low hydrogen donor concentrations will favor rearrangement and the ratios of iso-butyl acetate to t-butyl acetate should rise as the concentrations of the starting aldehyde are reduced.

As seen in Table II, the ratios of iso-butyl acetate to t-butyl acetate are dependent on the initial concentrations of aldehyde

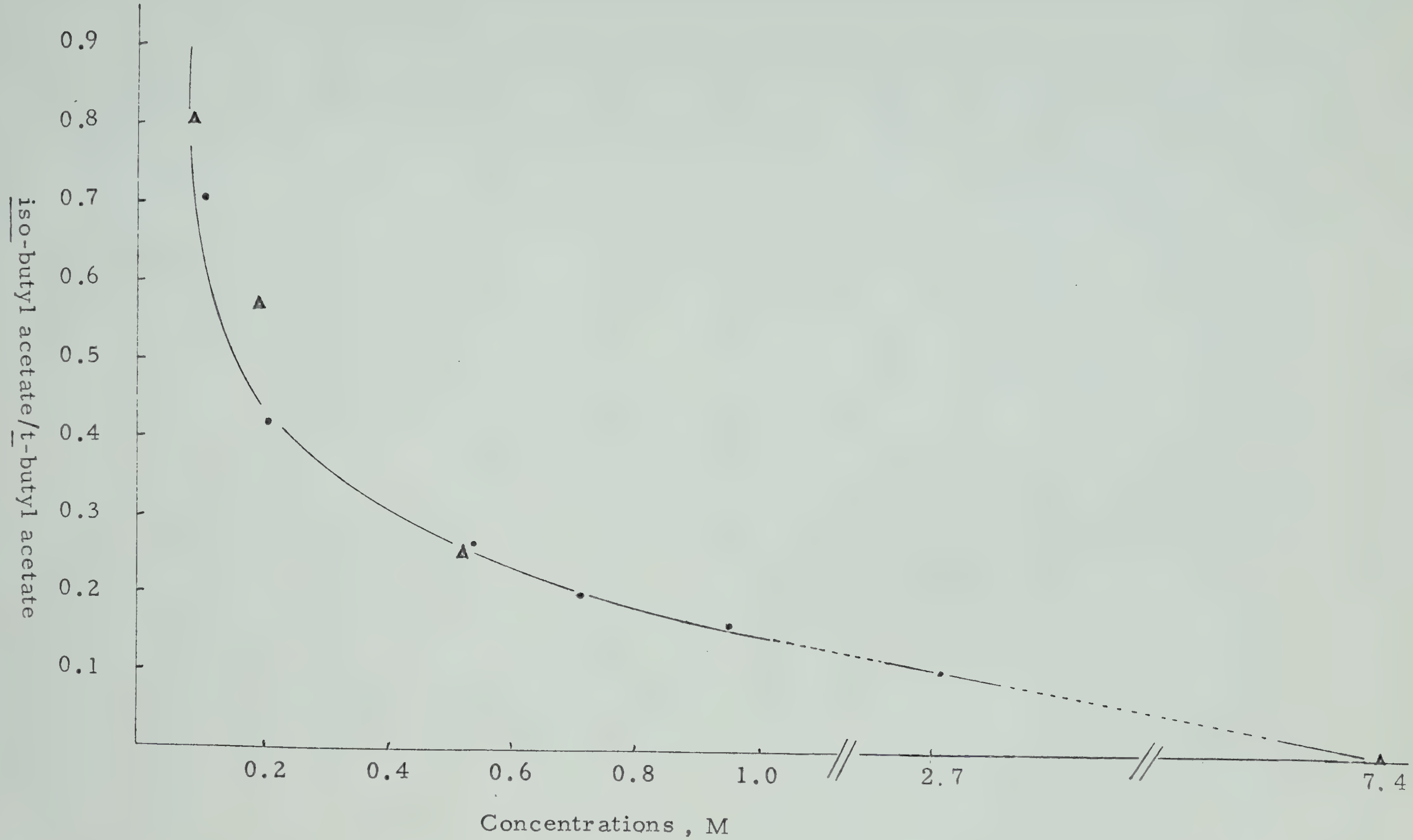
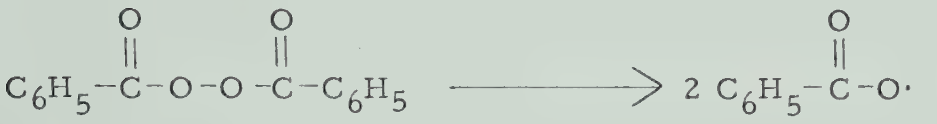


Figure 1. Plot of initial concentration of the aldehyde, 5, vs. product ratio of iso-butyl acetate/t-butyl acetate in peroxide initiated decomposition of 5.

benzene ● chlorobenzene ▲

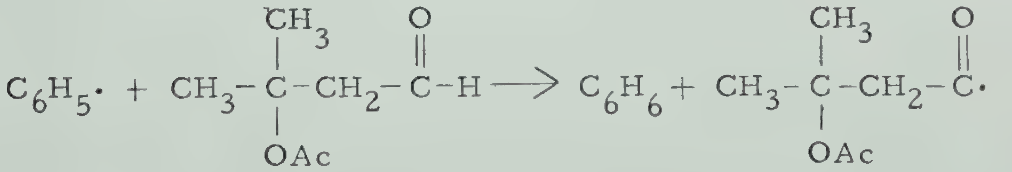
5. A plot of aldehyde initial concentrations versus the ratios of *iso*-butyl acetate to *t*-butyl acetate is shown in Figure 1. Low aldehyde concentrations favor the formation of *iso*-butyl acetate over *t*-butyl acetate. From these results, it is clear that these reactions cannot involve mode B as such an intermediate would yield the same ratio for all aldehyde concentrations. The intermediate must therefore be mode C since it favors rearrangement over hydrogen abstraction at low aldehyde concentrations.

On the basis of the results of this study, the following mechanism can be proposed as a general description of the free-radical 1,2 migration of acetoxy group.

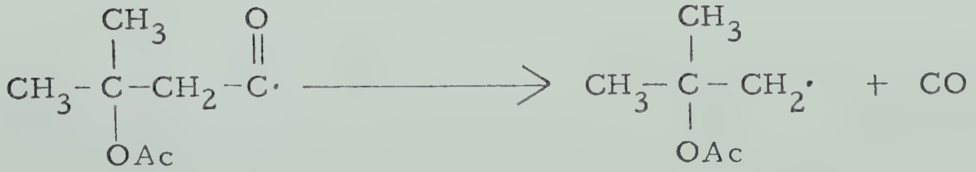


$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 \longrightarrow 2\ C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-O\cdot \qquad (E)$$

$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-O\cdot \longrightarrow C_6H_5\cdot + CO_2 \qquad (F)$$



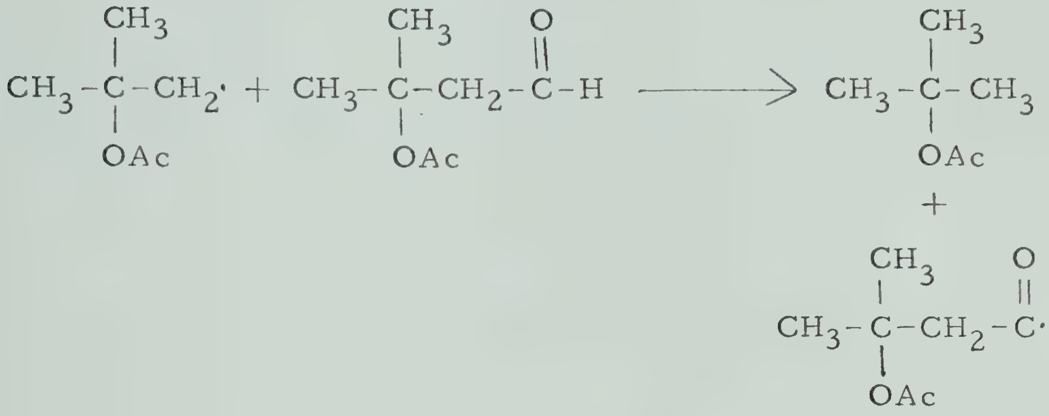
$$C_6H_5\cdot + CH_3-\underset{\underset{\displaystyle OAc}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H \longrightarrow C_6H_6 + CH_3-\underset{\underset{\displaystyle OAc}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}\cdot \qquad (G)$$



$$CH_3-\underset{\underset{\displaystyle OAc}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}\cdot \longrightarrow CH_3-\underset{\underset{\displaystyle OAc}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2\cdot + CO \qquad (H)$$

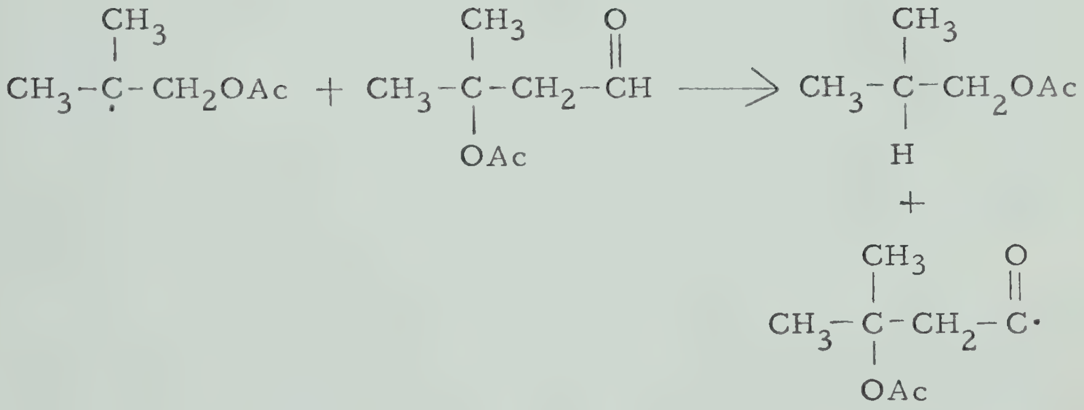
$$CH_3-\underset{OAc}{\overset{CH_3}{C}}-CH_2\cdot \longrightarrow CH_3-\underset{\bullet}{\overset{CH_3}{C}}-CH_2OAc$$

(I)



$$CH_3-\underset{OAc}{\overset{CH_3}{C}}-CH_2\cdot + CH_3-\underset{OAc}{\overset{CH_3}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-\underset{OAc}{\overset{CH_3}{C}}-CH_3 + CH_3-\underset{OAc}{\overset{CH_3}{C}}-CH_2-\overset{O}{\overset{\|}{C}}\cdot$$

(J)



$$CH_3-\underset{\bullet}{\overset{CH_3}{C}}-CH_2OAc + CH_3-\underset{OAc}{\overset{CH_3}{C}}-CH_2-\overset{O}{\overset{\|}{C}}H \longrightarrow CH_3-\underset{H}{\overset{CH_3}{C}}-CH_2OAc + CH_3-\underset{OAc}{\overset{CH_3}{C}}-CH_2-\overset{O}{\overset{\|}{C}}\cdot$$

(K)

No rearranged product is found in decarbonylation of aldehyde 6 (Table III) even in extremely dilute aldehyde concentration. This is unexpected because we would predict that radical 2 would rearrange in the same way as radical 1, since the stabilities of radicals decrease in the order 3° > 2° > 1°. Rearrangement occurs in radical 1 because the process involves the rearrangement of a primary radical to a more stable tertiary radical. In other

words, the stability of the tertiary radical provides part of the driving force for the rearrangement to occur. Curtin and Hurtwitze (85) has suggested that the factor which determines the fraction of rearranged product in decarbonylation is the rate of rearrangement compared to the rates of competing reactions of the unrearranged radical such as chain propagation by reaction with aldehyde or chain termination by dimerization or disproportionation. They conclude after studying the 1,2 rearrangements of four radicals that rearrangement can receive additional driving force by any change which stabilizes the rearranged radical or destabilizes the unrearranged radical with respect to the rearranged radical. Thus rearrangement does not occur in decarbonylation of the aldehyde, 6, may be due to the fact that radical 4 (secondary radical) is not as stable as radical 3 (tertiary radical). Consequently it does not provide enough driving force for the rearrangement to occur.

Triphenyltin hydride is a rather unstable, viscous liquid which reacts with atmospheric oxygen to give hexaphenyltin (86) and decomposes to tetraphenyltin and metallic tin on standing in sunlight. The original reports on the reduction of alkyl and aryl halides (87-89) by organotin hydrides have been followed by a number of papers concerning the scope and mechanism of the reaction. It is generally accepted that the reduction of simple halides proceeds by a free-radical chain mechanism (57) involving reactions M and N as chain-carrying steps and reactions O-Q as possible termination steps. Several lines of evidence support this formulation. The presence

$$(C_6H_5)_3SnH \ + \ Q\cdot \longrightarrow (C_6H_5)_3Sn\cdot \ + \ QH \qquad (L)$$

$$(C_6H_5)_3Sn\cdot \ + \ RX \longrightarrow R\cdot \ + \ (C_6H_5)_3SnX \qquad (M)$$

$$R\cdot \ + \ (C_6H_5)_3SnH \longrightarrow RH \ + \ (C_6H_5)_3Sn\cdot \qquad (N)$$

$$2 \ (C_6H_5)_3Sn\cdot \longrightarrow (C_6H_5)_3SnSn(C_6H_5)_3 \qquad (O)$$

$$R\cdot \ + \ (C_6H_5)_3Sn\cdot \longrightarrow RSn(C_6H_5)_3 \qquad (P)$$

$$2 \ R\cdot \longrightarrow R(+H) \ + \ R(-)H \text{ or } RR \qquad (Q)$$

of a tercovalent carbon intermediate can be adduced from the observations that optically active $\alpha$-phenylethyl chloride with triphenyltin deuteride yields racemic $\alpha$-deuterioethylbenzene; that $\alpha$- and $\gamma$-methylallyl chlorides each lead to formation of mixtures of 1-butene and <u>cis</u>- and <u>trans</u>-2-butenes; and that reduction of propargyl bromide leads to formation of both propyne (85%) and allene (15%) at 45° in the absence of a solvent (57). Evidence that the intermediate is a free radical follows from catalysis of the reaction by azobisisobutyronitrile, and from the fact that it can be retarded by hydroquinone.

Triphenyltin hydride is a good hydrogen donor and hydrogen transfer from triphenyltin hydride to organic radical intermediate is a fast process ($k \cong 10^4 - 10^6 \ M^{-1}sec^{-1}$) (90). Ingold and Carlsson (91) have shown that the absolute rate constant for hydrogen transfer from triphenyltin hydride to <u>t</u>-butyl radicals in $M^{-1}sec^{-1}$ is $5 \times 10^6$. This rate constant is of considerable

significance for it indicates the approximate rate of intramolecular processes of carbon free radicals for which triphenyltin hydride can be used as a probe. This is to say that if an intramolecular process (such as rotation about single bond or 1,2 migration) is much faster than the hydrogen transfer rate constant of triphenyltin hydride, the intermediate cannot be intercepted, but if the intramolecular process is of the same order of magnitude as k $[R_3SnH]$ or slower, then hydrogen transfer will occur more rapidly than this process, and trapping can be effected.

The fact that only unrearranged product is found in the reduction of the chloride, 7, can be interpreted by the rapid hydrogen transfer process of triphenyltin hydride. The initially formed radical 1 from reduction is intercepted by hydrogen transfer before the occurrence of rearrangement. The absence of rearranged product in the reduction of chloride 8 substantiates the results of decarbonylation of aldehyde 6. This can be explained by a combination of two factors. First, the initially formed radical is trapped by hydrogen transfer before rearrangement. Second, the secondary radical, 4, is not stable enough for rearrangement to occur (as discussed in detail before).

In summary, 1,2 acetoxy group migration occurs only in decarbonylation of the aldehyde, 5, presumably because the rearrangement involves the formation of a tertiary radical from a primary radical and is favored energetically. That no rearrangement is detected in decarbonylation of the aldehyde, 6, may be due

to the fact that a secondary radical is not stable enough for the process to occur. The absence of rearranged product in reduction of chlorides 7 and 8 can be rationalized by the interception of the initially formed radical before rearrangement or the relatively low stability of the secondary radical compared with the tertiary radical in the case of the chloride, 8.

# EXPERIMENTAL

## I. Materials and Reagents

### Solvents

n-Pentane was Eastman practical grade material. It was purified by vigorous stirring with portions of concentrated sulfuric acid until the acid layer remained colorless and was then distilled b.p. 30-32° (630 mm). Benzene was Shawinigan reagent grade material and was purified by repeated partial recrystallization. Chlorobenzene was supplied by Fisher Chemical Co. and was purified by spinning band distillation. Anhydrous ether was supplied by Mallinckrodt Chemical works.

### Reference compounds and standards

Authentic compounds, for use as glpc standards, for comparing retention times with those of reaction products, and for obtaining reference spectra, were reagent grade materials used as supplied with the exception of $\beta$-methylcrotonaldehyde which was prepared in exactly the same way as Burkhardt (92).

## II. Method and Procedures

### General procedure for reactions

Reaction ampoules were made of Pyrex tubes joined to 10/30 joints, the total volume being about 10 ml. The ampoules were cleaned with chromic acid, distilled water, concentrated

ammonia and finally distilled water and then oven-dried at 110°. In subdued light, the reaction mixture was added into the ampoules which were then degassed by three cycles of freeze-thaw at ca. $10^{-5}$ mm. After degassing, the ampoules were sealed under vacuum, allowed to warm and then equilibrated at the desired temperature. The ampoules containing aldehydes were put in a constant temperature water bath at 75°. The ampoules containing the chlorides were immersed in a constant low temperature bath at 0° and were irradiated by a 300-W projector lamp placed at a distance of three to four inches from the ampoules.

Gas liquid partition chromatograph (glpc)

For glpc analyses three instruments were used. The instruments and columns are described below. Throughout this work the glpc column support used was acid washed chromosorb W either 60/80 or 80/100 mesh.

(1) Varian Aerograph model 1520 with flame and thermal conductivity detectors. Two columns made of stainless steel were used.

(a) 10' by 1/8" Ucon Polar (50 HB 2000), 5%.

(b) 10' by 1/8" SF-96, 5%.

(2) Carlo Erba model GV with flame and thermal conductivity detectors. Five columns made of glass were used.

(a) 6 1/2' by 1/4" Ucon Polar, 10%.

(b) 6 1/2' by 1/4" SF-96, 3%.

(c) 13' by 1/4" Ucon Polar, 10%.

(d) 13' by 1/4" SF-96, 3%.

(e) 13' by 1/4" SE-30, 10%.

(3) Aerograph model 1200 Hy-Fi III connected to an A.E. I. MS12. Three columns made of stainless steel were used.

(a) 10' by 1/4" SE-30, 10%.

(b) 10' by 1/8" Ucon Polar, 5%.

(c) 10' by 1/8" SF-96, 5%.

Analyses were carried out in triplicate. Peak areas were measured either by multiplying peak height by peak width at one-half peak height, or by a planimeter if the peak did not resemble a Gaussian curve. The planimeter was supplied by Keuffel Esser Co. (Model 620022). The area ratio of the product to added bromobenzene as a standard was used to calculate the concentration of the product present by multiplying the area ratio with known amount of added bromobenzene. The area ratio was corrected by a calibration factor which was obtained by comparing the area ratio with the mole ratio of an accurately prepared solution of the authentic material and bromobenzene in the solvent used for the reaction. Retention time comparison and peak enchancement were obtained by the addition of authentic material to a portion of the sample and reanalysis by glpc. At least two columns were used to compare the retention time of each compound in the reaction mixture.

## Spectral measurement

Infrared (ir) spectra were recorded on a Perkin-Elmer Recording Infrared Spectrophotometer, Model 421 or Model 337. The nmr spectra are proton spectra. Chemical shift are expressed in $\tau$ units and are relative to tetramethylsilane (TMS, $\tau = 10.00$). The spectra were obtained on a Varian Associates A-60 instrument. Ultraviolet (UV) spectra were obtained on a Jasco Optical Rotatory Dispersion Recorder Model ORD/UV-5.

Mass spectra were obtained on an A.E.I. Model MS12 which was coupled directly to an Aerograph Model 1200 Hy-Fi III gas chromatograph by means of a Watson/Biemann helium separater. The total ion monitor acted as a chromatographic detector and drived a potentiometer recorder. Spectra could be scanned in 2-3 seconds and the output was on a high speed uv oscillographic recorder.

## Physical Constants

All boiling points are uncorrected. Refractive indices were measured on a Bausch and Lomb refractometer.

## Microanalyses

Microanalyses were performed in the microanalytical laboratory, Chemistry Department, University of Alberta, Edmonton.

## Preparations

### 2-Methyl-4-penten-2-ol, (10)

This was prepared by a modification of the method of Fischer (58). Magnesium turnings (50 g, 2 g. atom) under anhydrous ether (250 ml) were activated by the addition of a little allyl bromide. A mixture of 3-chloropropene (153 g, 2 moles) and pure acetone (116 g, 2 moles) in ether (250 ml) was added in portions to the swiftly stirred and ice-cooled suspension over 2 hr. Ice (200-400 g) was added cautiously to decompose the viscous reaction mixture. The ether layer was separated, dried ($K_2CO_3$), concentrated, and purified by distillation, giving 70% yield of the alcohol, 10: bp 112-115° (690 mm) [lit. (58) bp 117-119°]; ir (film) 1640, 2950, 3070 and 3400 cm$^{-1}$; nmr ($CDCl_3$) $\tau$4.10 (m, 1), $\tau$4.80 (m, 2), $\tau$7.50 (s, 1), $\tau$7.80 (d, 2, J = 7.5 cps), $\tau$8.80 (s, 6).

### 2-Methyl-4-penten-2-yl acetate, (9)

This was prepared by a modification of the method of Adams (93). A mixture of benzene (240 ml), the alcohol, 10 (76.2 g, 0.76 mole), sodium acetate (55.38 g, 0.68 mole), and acetic ahydride (163.2 g, 1.02 moles) was heated on a steam bath for 24 hours with stirring to prevent caking of sodium acetate. The reaction mixture was allowed to cool and was poured into cold water (1.0 liter). The upper layer was separated and allowed to stand for 2 hr over 5% sodium carbonate (500 ml) with frequent stirring. After washing with water (1.2 liters) the benzene was evaporated.

The residue was distilled under diminished pressure giving 40.2 g (37%) of the olefin, 9: bp 66-68° (143 mm); ir (film) 3090, 2980, 1750 and 1380 $cm^{-1}$; nmr ($CDCl_3$) $\tau$4.40 (m, 1), $\tau$4.80 (m, 2), $\tau$7.45 (m, 2), $\tau$8.00 (s, 3), $\tau$8.55 (s, 6).

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.60; H, 9.86. Found: C, 67.45; H, 9.87.

### β-Acetoxy-β-methylbutyraldehyde, (5)

A stream of ozone in oxygen was bubbled through a mixture of 9 (28.4 g, 0.2 mole) and pure ethyl acetate (80 ml) at -60° to -80° for 2.5 hr until a pale blue solution resulted. Ether (100 ml) was added and the ozonide was reduced immediately at 0° with zinc dust (20 g) and 50% acetic acid. The acid solution was added in small portions so that the temperature of the reaction mixture remained at between 10-20°. The slurry of zinc and zinc salts was filtered off and washed with small portions of ether. The combined extracts were washed with portions of 5% sodium bicarbonate (20 ml) then water until the aqueous layer was slightly basic; it was dried ($MgSO_4$), concentrated and distilled at reduced pressure, affording 20 g (70%) of the aldehyde, 5; bp 71-72° (13 mm); $n_D^{25}$ 1.4210; ir ($CCl_4$) 2980 and 1750 $cm^{-1}$; nmr ($CCl_4$) $\tau$0.25 (t, 1, J = 1.2 cps), $\tau$6.8 (d, 2, J = 1.3 cps), $\tau$7.9 (s, 3), $\tau$8.5 (s, 6).

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.33; H, 8.33. Found: C, 58.46; H, 8.51.

## 4-Penten-2-ol, (13)

The compound, 13, was prepared according to the procedure of Behnisch (94) with slight modification. In a 2-l three necked flask, fitted with a mechanical stirrer, a separatory funnel, and a dry ice-acetone condenser protected by a calcium chloride tube were placed magnesium turnings (73 g, 3 g atom) under dry ether (125 ml). A solution of 3-chloropropene (191.25 g, 2.5 moles) in dry ether (125 ml) was added through the separatory funnel at such a rate that the reaction mixture was maintained at reflux. The reaction mixture was then heated to reflux on a steam bath for 1 hr. The flask was cooled to -5° and a solution of acetaldehyde (100 g, 2.3 moles) in dry ether (125 ml) was added over a period of 1 hr at this temperature. After addition of the acetaldehyde, the product was decomposed with crushed ice (1 Kg). The basic magnesium halide was dissolved by addition of 15% sulfuric acid (0.5 l). The ether solution was separated, neutralized with saturated sodium bicarbonate solution, dried with magnesium sulfate, filtered, and fractionally distilled, giving 31 g (36%) of the alcohol, 13; bp 112-114° (735 mm) [lit. (90) bp 114-116° (740 mm)]; ir ($CCl_4$) 3080 and 3400 $cm^{-1}$; nmr ($CCl_4$) $\tau$4.2 (m, 1), $\tau$5.00 (m, 3), $\tau$6.0 (m, 1), $\tau$7.8 (m, 2), $\tau$8.8 (d, 3, J = 3.5 cps).

## 4-Penten-2-yl acetate, (14)

The acetate, 14, was prepared according to the procedure by Hauser (72) with modification. In a three necked 1-l flask

equipped with a reflux condenser, mercury sealed stirrer, and a dropping funnel were placed the alcohol, 13 (43.0, 0.5 mole), N,N-dimethylaniline(70.3 g, 0.58 mole), and dry ether (100 ml). The solution was heated to reflux and acetyl chloride (41.6 g, 0.53 mole) was added to the stirred solution at such a rate that moderate reflux continued after the source of heat was removed. After the addition was completed, the mixture was heated on a steam bath for 1 hr, cooled to room temperature, dissolved in water (40 ml), and stirred until all solid material had dissolved. The ether layer was separated and extracted with portions (50 ml) of cold 10% sulfuric acid until the extract did not become cloudy when basified. After a final washing with saturated sodium bicarbonate (25 ml), the ether solution was dried with anhydrous sodium sulfate (4 g), allowed to stand over Drierite (10 g) overnight, filtered, concentrated, and distilled. The yield was 50%: bp 129-131° (698 mm); ir ($CCl_4$) 1730 and 3080 $cm^{-1}$; nmr ($CCl_4$) $\tau$4.20 (m, 1), $\tau$5.00 (m, 3), $\tau$7.80 (m, 2), $\tau$8.05 (s, 3), $\tau$8.80 (d, 3).

Anal. Calcd for $C_5H_{10}O$: C, 65.63; H, 9.37. Found: C, 65.61 H, 9.34.

### $\beta$-Acetoxybutyraldehyde, (6)

The preparation of $\beta$-acetoxybutyraldehyde, (6), from olefin 14 followed exactly the procedure for the preparation of the aldehyde, 5, from the olefin, 9. The yield was 55%: bp 66-67° (10 mm); $n_D^{25}$ 1.4183 [lit. (60) bp 70-72° (12 mm)] ; ir (film)

1470 and 1730 $cm^{-1}$; nmr ($CCl_4$) $\tau$1.45 (t, 1), $\tau$4.75 (q, 1), $\tau$7.40 (m, 2), $\tau$8.00 (s, 3), $\tau$8.70 (d, 3, J = 2.5 cps).

### 1-Chloro-2-methyl-2-propanol, (15)

This was prepared by a modification of the method of Palomaa and Kaski (74). In a three necked flask, equipped with a pressure-equalizing dropping funnel were placed magnesium turnings (24 g, 1 g atom) and anhydrous ether (250 ml). An ice cold mixture of methyl bromide (100 g, 1.05 moles) in anhydrous ether (500 ml) was added dropwise with stirring and the reaction started spontaneously. The methyl bromide was added at such a rate that the solution boiled gently under reflux. After the stirred solution of methylmagnesium bromide was cooled to 0°, a solution of ethyl chloroacetate (30.50 g, 0.25 mole) in dry ether (50 ml) was added slowly. The mixture was then placed on a steam bath and boiled under reflux for 1 hr. The mixture was cooled and the intermediate was decomposed with ice (200-400 g). After the separation of the organic layer, the aqueous layer was washed with small portions of ether. The combined ether extracts were washed with water, 5% sodium carbonated and again with water, dried ($MgSO_4$), concentrated and distilled, affording 26 g (95%) of 15: bp 125-127° (690 mm) [lit. (95) bp 128]; ir (flim) 780 and 3400 $cm^{-1}$; nmr ($CCl_4$) $\tau$5.90 (s, 1), $\tau$6.55 (s, 2), $\tau$8.70 (s, 6).

## 1-Chloro-2-methyl-2-propyl acetate, (7).

The synthesis of compound 7 followed exactly the procedure used for the preparation of the acetate, 14. The yield was 28 g (50%): bp 64-65° (4 mm); $n_D^{24}$ 1.4237 [lit. (74) bp 24-25.5° (2.5 mm), $n_D^{20}$ 1.42368]; ir (film) 780 and 1750 $cm^{-1}$; nmr ($CCl_4$) $\tau$6.24 (s, 2), $\tau$8.05 (s, 3), $\tau$8.52 (s, 6).

## 1-Chloro-2-propyl acetate, (8)

This experiment followed exactly the procedure used for the preparation of olefin 9 from alcohol 10 except that 1-chloro-2-propanol was the alcohol. The yield was 45%: bp 82-83° (38 mm); $n_D^{24}$ 1.4225 [lit. (96) bp 147-149° (745 mm), $n_D^{20}$ 1.4223]; ir ($CCl_4$) 770, 1240, 2370 and 1750 $cm^{-1}$; nmr $\tau$5.0 (m, 1), $\tau$6.4 (d, 2, J = 6 cps), $\tau$8.0 (s, 3), $\tau$8.7 (d, 3, J = 7 cps).

## Triphenyltin hydride

Triphenyltin hydride was prepared according to the procedure of Kuivila (73) with modification. Lithium aluminum hydride (1.56 g, 0.04 mole) and triphenyltin chloride (38.50 g, 0.10 mole) were added to anhydrous ether (150 ml) in a three necked flask equipped with a dropping funnel, a stirrer, and a reflux condenser equipped with a balloon filled with nitrogen gas. The mixture was stirred for 15 minutes and then at room temperature for 3 hr. It was then cooled to 0° and ice cold water (100 ml) was added slowly. The ether layer was washed with two portions (100 ml) of ice cold water and dried over magnesium sulfate. After

evaporation of ether, the crude product was distilled very rapidly in vacuo using an oil bath pre-heated to 200°. The yield amounted to 29 g (85%): bp 164-168° (0.5 mm) [lit. (73) bp 162-168° (0.5 mm)].

Peroxide-initiated reaction of β-acetoxy-β-methylbutyraldehyde, 5. (Reactions 1-15).

A. (Reactions 1-6) An accurately prepared solution of 5 (0.7 M) in benzene (10 ml) was divided into two equal portions. The first portion was transferred to an ampoule containing benzoyl peroxide (100 mg, 0.40 mmole), degassed in the dark, sealed under vacuum and allowed to stand in a constant temperature bath at 75° for 3 days. The second portion was stored in the refrigerator to serve as a control.

After being cooled to 77°K the ampoules were opened and bromobenzene (117 mg, 0.74 mmole) was added as a glpc standard. Glpc analysis (model 1520, 10' Ucon Polar 80°) indicated the presence of unreacted starting material, acetic acid, t-butyl acetate and iso-butyl acetate in quantities shown in Table I. In separate experiments authentic samples of the products were subjected to the same reaction conditions and were found to be completely stable.

B. (Reactions 11, 13 and 15) Accurately prepared solutions of 5 (1.07-5.02 mmole, see Table II) in chlorobenzene (10 ml) were divided into two equal portions by transferring 5 ml aliquots into ampoules containing benzoyl peroxide (100 mg, 0.4 mmole). The

second portions were stored as controls. The ampoules were degassed, sealed, and immersed in a constant temperature water bath at 75° for 3 days.

Glpc analysis on two columns (model 1520, 10' Ucon Polar and 10' SF-96, 70°) indicated that all samples contained unreacted starting material, t-butyl acetate, iso-butyl acetate, and acetic acid (except in reaction 15). In order to separate all the compounds present in the reaction mixture, a 10' SF-96 column was used to analyse t-butyl acetate and iso-butyl acetate. All other products were analysed with a 10' Ucon Polar column. Less than 50% of the starting material was accounted for as products and unreacted aldehyde in any reaction (Table II). Decarbonylation of a concentrated solution of compound 5 (7.4 M) was also carried out. t-Butyl acetate and acetic acid were identified as the products yielded in the reaction.

C. (Reactions 7-10, 12, and 14) These were done under the same conditions as in section B (reactions 11, 13, and 15) except that benzene was used as the solvent.

Glpc analysis on four columns (model GV, 13' Ucon Polar, 13' SF-96, 6 1/2' SF-96, and 13' SE-30) showed the presence of β-methylcrotonaldehyde in addition to the products observed in reactions 11, 13, and 15. Again, t-butyl acetate and iso-butyl acetate were analysed with a 13' SF-96 column and other compounds were analysed with a 13' Ucon Polar column. β-Methylcrotonaldehyde and the unreacted aldehyde, 5, were collected by glpc from reaction 7 and their ir and nmr spectra were found to be identical to the spectra of the authentic compounds. Reaction 10 was again analysed

by glpc (model 1200, 10' SE-30, 10' SF-96) connected to an A.E.I. MS12. Mass spectra of the product peaks were found to be identical to authentic compounds analysed under the same conditions. 95%, 98%, 94%, 91%, 62%, and 55% of the starting material were found as products and unreacted aldehyde, 5, in reactions 7, 8, 9, 10, 12, and 14 respectively (see Table II).

Peroxide-initiated reaction of β-acetoxybutyraldehyde, (6). (Reactions 16-18)

These were done in exactly the same way as reactions 11, 13, and 15 except that the concentrations of the aldehyde were different (see Table III).

Crotonaldehyde, acetic acid, and iso-propyl acetate (see Table III) were shown to be present by glpc analysis on two columns (model GV, 13' SF-96, 6 1/2' Ucon Polar). The order of elution was iso-propyl acetate, crotonaldehyde, acetic acid, and the unreacted aldehyde in the 6 1/2' Ucon Polar column. Reaction 16 was also analysed by glpc (model 1200, 10' SF-96) connected to an A.E.I. MS12. Mass spectra of the product peaks were found to be identical to those of authentic compounds. Reactions 16-18 were then combined, concentrated, and collected for crotonaldehyde by glpc (model GV, 6 1/2' Ucon Polar). The nmr spectra of the collected sample and the authentic material were found to be identical. 78%, 79%, and 88% of the starting aldehyde was accounted for as products and unreacted starting material in reactions 16, 17, and 18

respectively.

Photo-initiated reduction of 1-chloro-2-methyl-2-propyl acetate, (7), with triphenyltin hydride. (Reactions 19-22)

A. Aliquots, 5 ml, of accurately prepared solutions of the chloride, 7 (0.19 - 1.34 x $10^{-2}$ M, see Table IV) in n-pentane (10 ml) were added to ampoules containing azobisisobutyronitrile (ca. 4 mole %) and triphenyltin hydride (77.10 - 66.56 x $10^{-2}$ M). The other 5 ml portions were stored in the refrigerator as controls. The ampoules were degassed and sealed in vacuo and were then immersed in a constant low temperature bath maintained at $0^{o}$ and irradiated for 7 days by a 300-W projector lamp.

Glpc analysis on two columns (model GV, 13' SF-96 and 6 1/2' Ucon Polar) showed that t-butyl acetate and unreacted chloride were present in the reaction mixture. The order of elution on both columns was n-pentane, t-butyl acetate and unreacted chloride 7. Reactions 19-22 were combined, concentrated, separated by glpc and collected into an infrared cell equipped with a frustrated internal reflection optical flat (used to obtain spectrum even with extremely small amount of sample). The infrared spectra of the product and starting acetate were identical to those of authentic compounds analysed under the same conditions. The starting acetate, 83%, was accounted for as t-butyl acetate and unreacted acetate 7 in reaction 20 (see Table IV).

In separate experiments, t-butyl acetate and iso-butyl acetate were subjected to the similar reaction conditions (400-W clear tungsten bulb at 5° for 7 days) and were found to be completely stable. t-Butyl acetate (105%) and iso-butyl acetate (100%) were recovered after the reactions.

B. A 300 ml three necked flask was equipped with a reflux condenser, a nitrogen inlet and outlet tube, and a magnetic stirring bar. Into the flask was placed the acetate, 7 (1.05 g, 0.007 mmole), AIBN (11.6 mg, 0.07 mmole), and n-pentane (50 ml). Triphenyltin hydride (2.21 g, 0.007 mmole) in n-pentane (200 ml) was added dropwise at a rate of two drops per minute. The flask was immersed in a bath maintained at 20°, the nitrogen sweep was begun, the stirrer was started, and irradiation by 400-W clear tungsten bulb was commenced. This was allowed to react for five days, whereupon the reaction mixture was analysed by glpc (model GV, 6 1/2' Ucon Polar). t-Butyl acetate and unreacted acetate, 7, were found to be present in the reaction mixture.

Photo-initiated reduction of 1-chloro-2-propyl acetate,(8), with triphenyltin hydride. (Reactions 23-26)

These were carried out in the same way as reactions 19-22. Aliquots, 5 ml, of the chloride, 8 ($0.16 \times 10^2$ M) in n-pentane (10 ml) solutions were added to ampoules containing various concentrations of triphenyltin hydride ($1.01 - 27.67 \times 10^2$ M), see Table V, with azobisisobutyronitrile (ca. 4%). The other 5 ml portions were

stored as controls. The ampoules were degassed and sealed under vacuum as before. They were then irradiated at 0° for 7 days by a 300-W projection lamp. Glpc analysis on two columns (model GV, 13' SF-96 and 6 1/2' Ucon Polar) indicated the presence of iso-propyl acetate and unreacted chloride. The starting chloride, 97%, was accounted for as iso-propyl acetate and unreacted starting material in reaction 23.

### Attempted peroxide-initiated reaction of acetic acid and iso-butylene.

An accurately prepared solution of bromobenzene (65.9 mg, 0.42 mmole), acetic acid (44.0 mg, 0.63 mmole), and benzoyl peroxide (0.1 mg, 0.4 mmole) in benzene (15 ml) was placed in a 100 ml round bottom flask with a break seal. The solution was degassed in the dark, and iso-butylene (0.74 mmole, its volume was measured by a Töpler pump) was transferred into the flask which was sealed and immersed in a constant temperature bath at 75° for 3 days.

The gaseous material in the reaction mixture was measured by a Töpler pump and then analysed by mass spectrometry. iso-Butylene and carbon dioxide were identified as the gases present and 121% of the starting iso-butylene was recovered. Glpc analysis (model GV, 6 1/2' Ucon Polar) of the liquid part of the reaction mixture showed that acetic acid (108%) was recovered, and that no other compounds were present.

### Attempted reduction of 1-chloro-2-methyl-2-propyl acetate, (7) without AIBN.

The reaction mixtures were prepared in exactly the same way as reactions 19-22 without the addition of AIBN. The ampoules were then irradiated by ultraviolet light (quartz ampoules were used) or a 300-W projection lamp at various temperatures for 2-3 days. Glpc analysis (model GV, 13' SF-96) showed that no reduction of the acetate, 7, occurs and all the starting acetate was recovered.

# BIBLIOGRAPHY

1. P. Mayo, "Molecular Rearrangement", Interscience Publishers, New York, N. Y., 1963, p. 1 - 232.
2. C. Walling, "Free Radicals in Solution", John Wiley and Sons, Inc., New York, N. Y., 1963, p. 269.
3. E. S. Gould, "Mechanism and Structure in Organic Chemistry", Holt, Rinehardt, and Winston, New York, N. Y., 1959, p. 755.
4. G. H. Williams, "Advances in Free-Radical Chemistry", Logos Press, London, 1965, p. 211.
5. H. H. Glazebrook and T. G. Pearson, J. Chem. Soc., 1777 (1936).
6. M. S. Kharasch, S. S. Kane, and H. C. Brown, J. Am. Chem. Soc., 63, 526 (1941).
7. C. R. Masson, J. Am. Chem. Soc., 74, 4731 (1952).
8. H. T. J. Chilton and B. G. Gowenlock, Trans. Faraday Soc., 49 (1953).
9. C. A. Heller and A. S. Gordon, J. Phy. Chem., 60, 1315 (1956).
10. B. H. M. Billinge and B. G. Gowenlock, J. Chem. Soc., 3252 (1962).
11. M. S. Kharasch, F. L. Lambert, and W. H. Urry, J. Org. Chem., 10, 298 (1945).
12. L. H. Slaugh, J. Am. Chem. Soc., 81, 2262 (1960).
13. D. Y. Curtin and J. C. Kauer, J. Org. Chem., 25, 880 (1960).
14. H. C. Brown and G. A. Russell, J. Am. Chem. Soc., 74, 3995 (1952).

15. V. V. Voevodsky, T. K. Lavrovskaya, and R. E. Mardaleishvily, Dokl. Akad. Nauk SSSR, 81, 215 (1951).

16. M. S. Kharasch, M. Weiner, W. Nudenberg, Amma Bhattacharya, Wang Ting-I, and N. C. Tang, J. Am. Chem. Soc., 83, 3232 (1961).

17. C. C. Lee and D. G. Lee, Can. J. Chem., 38, 2315 (1960).

18. F. C. Whitemore, A. N. Popkin, H. J. Bernstein, and J. P. Wilkins, J. Am. Chem. Soc., 63, 124 (1941).

19. W. H. Urry and N. Nicolaides, J. Am. Chem. Soc., 74, 5163 (1952).

20. F. H. Seubold, J. Am. Chem. Soc., 75, 2532 (1953).

21. M. S. Kharasch, Y. C. Liu, and W. Nuderberg, J. Org. Chem., 20, 680 (1955).

22. C. Walling, "Free Radicals in Solution", John Wiley and Sons Inc., New York, N. Y., 1963, p. 373.

23. J. D. Backhurst, J. Chem. Soc., 3497 (1959).

24. J. A. G. Dominiguez and A. F. Trotman-Dickenson, J. Chem. Soc., 940 (1962).

25. L. H. Slaugh, J. Am. Chem. Soc., 87, 1522 (1965).

26. A. N. Nesmeyanov, R. Kh. Freidlina, and V. I. Firstov, Izv. Akad. Nauk, Otd. Him. Nauk, 505 (1951).

27. A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, Dokl. Akad. Nauk SSSR, 81, 199 (1951).

28. V. N. Kost, T. T., Sidorova, R. Kh. Freidlina, and A. N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 132, 606 (1960).

29. A. N. Nesmeyanov, R. Kh. Freidlina, and A. B. Belyavsky, Izv. Akad. Nauk SSSR, Otd. Him. Nauk, 1028 (1959).

30. R. Kh. Freidlina, V. N. Kost, M. Ya. Khorlina, and A. N. Nesmeyanov, Dok. Akad. Nauk SSSR 137, 341 (1961).

31. R. Kh. Freidlina, M. Ya. Khorlina, and A. N. Nesmeyanov, Izv. Akad. Nauk SSSR, Otd. Him. Nauk, 658 (1960).

32. V. N. Kost, T. T. Vasilyeva, and R. Kh. Freidlina, Dok. Akad. Nauk Beloruss SSR, 7, 614 (1963).

33. M. S. Kharasch, E. H. Rossin, and E. K. Fields, J. Am. Chem. Soc., 63, 2558 (1941).

34. R. Kh. Freidlina, A. N. Nesmeyanov, R. G. Petrova, and A. B. Terentiev, Dokl. Akad. Nauk SSR, 127, 575 (1959).

35. A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharin, Dokl. Akad. Nauk SSSR 81, 199 (1951).

36. R. Kh. Freidlina, A. B. Terentiev, R. G. Petrova, and A. N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 138, 859 (1961).

37. W. H. Urry and J. R. Eiszner, J. Am. Chem. Soc., 74, 5822 (1952).

38. W. H. Urry, J. R. Eiszner, and J. W. Wilt, J. Am. Chem. Soc., 79, 918 (1957).

39. C. Walling, "Free Radicals in Solution", John Wiley and Sons Inc., New York, N. Y. 1963 pp. 426.

40. P. S. Skell, R. G. Allen, and N. G. Gilmour, J. Am. Chem. Soc., 83, 504 (1961).

41. W. O. Haag and E. I. Heiba, Tetrahedron Letters 41, 3683 (1965).

42. M. S. Kharasch, F. L. Lambert, and W. H. Urry, J. Org. Chem., 10, 298 (1945).

43. S. Winstein and F. H. Seubold, Jr., J. Am. Chem. Soc., 69, 2916 (1947).

44. W. H. Urry, D. J. Trecker, and H. D. Hartzler, J. Org. Chem., 29, 1663 (1964).

45. W. H. Urry and N. Nicolaides, J. Am. Chem. Soc., 74, 5163 (1952).

46. L. H. Slaugh, J. Am. Chem. Soc., 81, 2262 (1959).

47. W. B. Smith and J. D. Anderson, J. Am. Chem. Soc., 82, 656 (1960).

48. S. Winstein, R. Heck, S. Lapporte, and K. Baird, Experientia, 12, 138 (1956).

49. J.W. Wilt and H. Philip, J. Org. Chem., 25, 891 (1960).

50. M. S. Kharasch and H. C. Brown, J. Am. Chem. Soc., 61, 2142 (1939).

51. C. Ruechardt and H. Trautwein, Chem. Ber. 96, 160 (1963).

52. C. Ruechardt and E. Sieglinde, Chem. Ber. 95, 1921-42 (1962).

53. L. K. Montgomery, J. Matt, and J. R. Webster, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p. 29-N.

54. L. H. Slaugh, J. Am. Chem. Soc., 87, 1522 (1965).

55. D. H. R. Barton, H. Reimann, A. S. Capomaggi, T. Strauss, and E. P. Oliveto, J. Am. Chem. Soc., 83, 4481 (1961).

56. W. Reusch, C. K. Johnson and J. A. Manner, J. Am. Chem. Soc., 88, 2803 (1966).

57. H. G. Kuivila and L. W. Menapace, J. Am. Chem. Soc., 86, 3047 (1964).

58. F. G. Fischer, Chem. Ber. 76, 734 (1943).

59. E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, and W. Vaughan, Faraday Society Discussion no. 10, 242 ff and 315 (1951).

60. E. Späth and T. Meinhard, Chem. Ber. 76, 509 (1943).

61. C. T. Mason, C. W. R. Wade, and H. W. Pouncy Jr., J. Am. Chem. Soc., 76, 2255-6 (1954).

62. L. P. Kyriakides, J. Am. Chem. Soc., 36, 532 (1914).

63. V. Grignard and P. Abelmann, Bull. Soc. Chim. Fr. (4) 7, 638 (1910).

64. C. D. Hurd and J. L. Abernethy, J. Am. Chem. Soc., 63, 1966 (1941).

65. M. Bergmann and E. Kann, Ann., Chem., Justus Liebigs, 438, 278 (1924).

66. M. Backes. Compt. rend., 207, 74-6 (1938).

67. C. A. Kohn and W. Trantom, Sitzber, Akad. Wiss., Wien, IIb, 108, 744 (1899).

68. M. Bergmann, A. Miekely, and E. Von Lippmann, Chem. Ber. 62B, 1467 (1929).

69. M. Hori, J. Agr. Chem. Soc., Japan 17, 1 (1941).

70. R. H. Saunders, M. J. Murray, F. F. Cleveland, and V. I. Komarewsky, J. Am. Chem. Soc., 65, 1311 (1943).

71. V. S. Batalin and S. E. Slavina, J. Gen. Chem. (U.S.S.R.), 7, 202 (1937).

72. C. R. Hauser, B. E. Hudson, B. Abramovitch, and I. C. Shivers, Org. Syn., Coll. Vol. 3, 142 (1955).

73. H. G. Kuivila and O. F. Bennel, J. Am. Chem. Soc., 83, 1246 (1961).

74. M. H. Palomaa and T. K. Kaski, Suomen Kemistilehti, 17B, 7-9 (1944).

75. B. V. Barbour and S. J. Cristol, J. Am. Chem. Soc., 90, 2832 (1968).

76. H. G. Kuivila and L. W. Menapace, J. Org. Chem., 28, 2165 (1963).

77. R. K. Ingham, S. D. Rosenberg, and H. Gilman, Chem. Rev., 60, 507 (1960).

78. W. Braun, L. Rajbenbach, and E. R. Eirich, J. Phys. Chem., 66, 1591 (1961).

79. P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N. Y., 1953, p. 121.

80. J. C. Martin, J. W. Taylor, and E. H. Drew, J. Am. Chem. Soc., 89, 129 (1967).

81. H. J. Shine and J. R. Slagle, J. Am. Chem. Soc., 81, 6309 (1959).

82. D. C. Tuleen, P. D. Readio, and P. S. Skell, J. Am. Chem. Soc., 85, 2849 (1963).

83. J. Warkentin and E. Sanford, J. Am. Chem. Soc., 90, 1667 (1968).

84. P. Mayo, "Molecular Rearrangement", Interscience Publishers, New York, N. Y., 1963, p. 427-431.

85. D. Y. Curtin and M. J. Hurwitze, J. Am. Chem. Soc., 74, 5381 (1952).

86. R. F. Chambers and P. C. Hurwitze, J. Am. Chem. Soc., 83, 1246 (1961).

87. G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, J. Appl. Chem., 7, 356 (1957).

88. J. G. Noltes and G. J. M. van der Kerk, "Functionally Substituted Organotin Compounds", Tin Researach Institute, Greenford, England, 1956, pp. 72.

89. J. G. Noltes and G. J. M. van der Kerk, Chem. Ind. (London), 294 (1959).

90. H. G. Kuivila, Account of Chemical Research 10, 302 (1968).

91. D. J. Carlsson and K. U. Ingold, J. Am. Chem. Soc., 90, 1055 (1968).

92. Burkhardt, Heilborn, and Aldersley, British Chem. Abstr., B, 1212 (1939).

93. R. Adams and C. G. Ganerke, Org. Syn., Coll. Vol. 1, 279 (1955).

94. K. H. Slotta and R. Behmisch, Chem. Ber. 68B, 754-61 (1935).

95. A. Michael and V. L. Leighton, Chem. Ber. 39, 2789 (1906).

96. C. F. Irwin and G. F. Hennion, J. Am. Chem. Soc., 63, 859 (1941).